# Iridium-Catalyzed Asymmetric Intramolecular Allylic Amidation

Teichert, Johannes F.; Fañanás-Mastral, Martín; Feringa, Bernard

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Supporting Information



69451 Weinheim, Germany

# Iridium-Catalyzed Asymmetric Intramolecular Allylic Amidation: Enantioselective Synthesis of Chiral Tetrahydroisoquinolines and Saturated Nitrogen Heterocycles**

*Johannes F. Teichert, Martín Fañanás-Mastral, and Ben L. Feringa**

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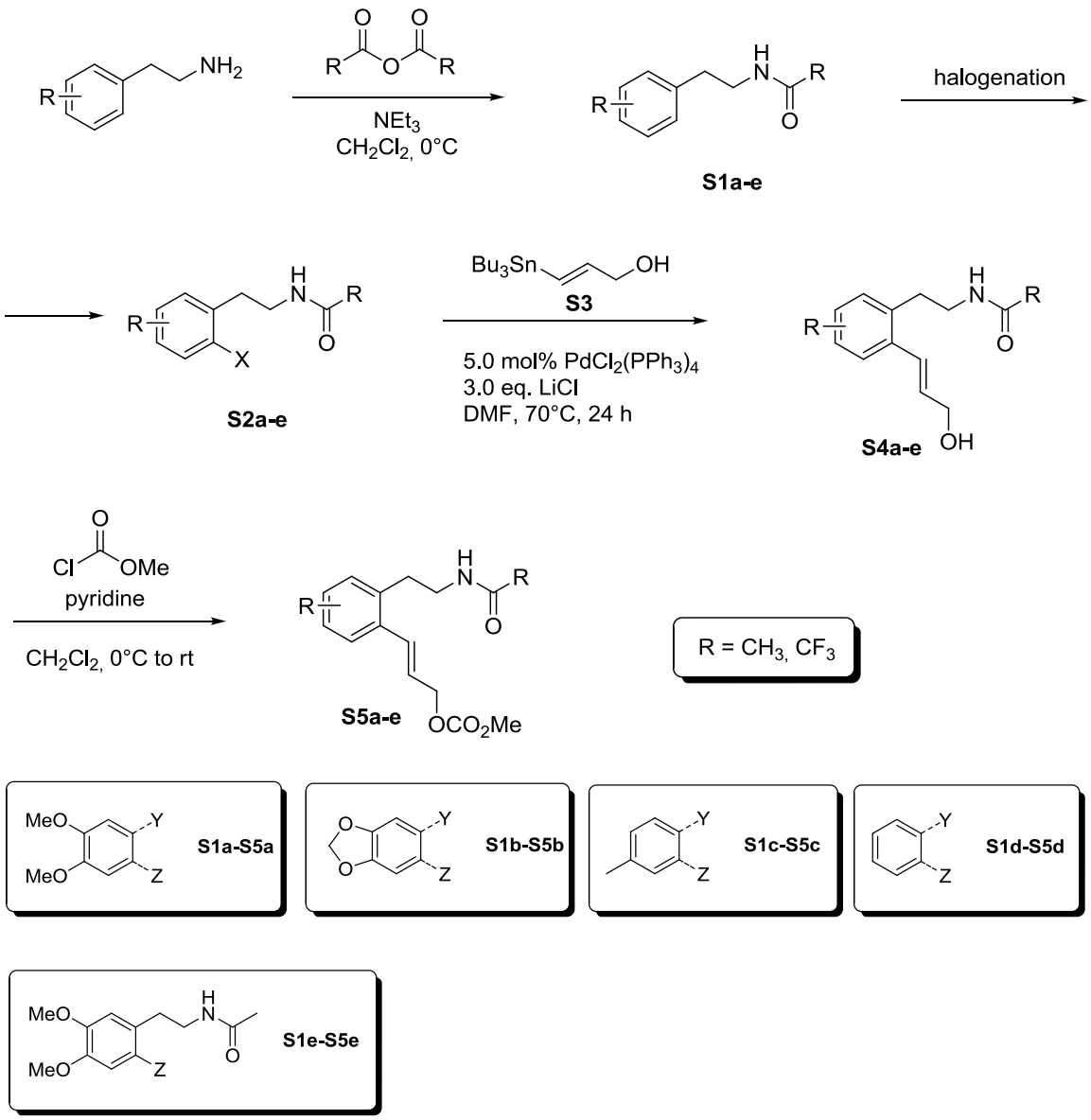
# Supporting Information

## 1.) General

Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60,0.25 mm. Components were visualized by UV and cerium/molybdenum staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890: MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). Mass spectra were recorded on a AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). $^{1}H$, $^{19}F$ and $^{13}C$-NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively), a Varian VXR300 (300 and 75 MHz, respectively) or a Varian Gemini 200, using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for $^{1}H$, δ 77.0 for $^{13}C$). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Optical rotations were measured on a *Schmidt + Haensch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Enantiomeric excesses (*ee* values) were determined by HPLC analysis using a Shimadzu LC-10AD*VP* HPLC equipped with a Shimadzu SPD-M10A*VP* diode array detector and chiral columns as indicated. *Ee*s were determined by comparison with the corresponding chiral compounds or the mixtures of both R and S enantiomers. All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. $CH_2Cl_2$ was dried and distilled over calcium hydride, THF and $Et_2O$ were dried and distilled over Na/benzophenone. Toluene was dried and distilled over Na. $[Ir(COD)Cl]_2$ was purchased from Strem Chemicals, Inc. . Complex **3** was prepared according to literature.[1, 2] Ligand **L1** was prepared according to literature.[3] Ligand **L2** was prepared according to literature.[4] Substrate **S3** was prepared according to literature.[5] Substrate **S7** was prepared according to literature.[6]

## 2.) Synthesis of Starting Materials

## 2.1.) Starting Materials for Tetrahydroisoquinoline synthesis

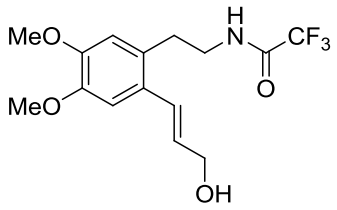



**General trifluroacetylation/acetylation protocol:**
To a solution of the corresponding amine (1.0 eq.) and $NEt_3$ (2.0 eq.) in $CH_2Cl_2$ (2 mL/mmol) was added dropwise trifluoroacetic anhydride (1.2 eq.) (or acetic anhydride in the case of **S1e**) at 0 °C. The mixture was stirred at this temperature for 1 h. The reaction was quenched with water (10 ml) and the mixture extrated with $CH_2Cl_2$ (3 x 5mL). The combined organic layers were washed with brine, dried over $Na_2SO_4$ and concentrated under vacuum to afford the corresponding *N*-trifluoroacetyl or *N*-acetyl compound. The products were used without further purification.

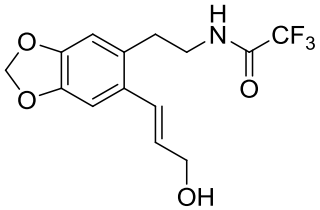
**Preparation of Substrates S1a-e**
Substrate **S2a** (X = I) was synthesized following literature procedures.[7] Substrate **S2b** (X = I) was prepared following the general trifluoroacetylation protocol (see above) from

2-(2-iodo-3,4-methyldioxyphenyl)ethylamine which was made following literature procedures.[6] **S2c** (X = I) was synthesized from **S1c** using $IPy_2BF_4$ (which was recrystallized from $CH_2Cl_2/Et_2O$ before use) as iodinating agent following a literature procedure.[8] Substrate **S2d** (X = Br) was prepared following the general trifluoroacetylation protocol (see above) from commercial 2-bromophenethylamine. S2e was synthesized following the same procedure as for **S2a**[7], but with *N*-acetylation instead of *N*-trifluoroacetylation (see general procedure above).

**General procedure for the synthesis of substrates S4 (Stille coupling with S3):**
To a mixture of iodide **S2** (1.0 eq.), *E*-β-tributylstannylpropenol **S3** (1.2 eq.) and lithium chloride (3.0 eq.) in dry DMF (6 mL/mmol), bis(triphenylphosphine)palladium dichloride (5.0 mol%) was added under nitrogen atmosphere. The resulting solution was stirred at 70 °C for 16 h. After cooling to room temperature, the mixture was diluted with ethyl acetate (15 mL/mmol) and washed with water (4 x 10 mL/mmol). The organic layer was dried with $Na_2SO_4$ and concentrated under vacuum. Purification by column chromatography afforded **S4** as white solids.

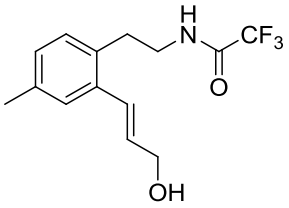



(*E*)-2,2,2-Trifluoro-*N*-(2-(3-hydroxyprop-1-enyl)-4,5-dimethoxyphenethyl)acetamide **S4a**
Following the general procedure, 274 mg of **S4a** (0.83 mmol, 83%) were isolated from the reaction of iodide **S2a** (403 mg, 1 mmol) after purification by column chromatography using ethyl acetate/pentane 3:1 as eluent.
$^1$H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.93 (br s, 1H), 6.80 (dt, *J* = 15.6, 1.4 Hz, 1H), 6.60 (s, 1H), 6.17 (dt, *J* = 15.6, 5.4 Hz, 1H), 4.31 (dd, *J* = 5.4, 1.6 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.48 (q, *J* = 6.7, 2H), 2.89 (t, *J* = 6.7, 2H), 2.52 (br s, 1H).
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.4 (q, *J* = 37.0 Hz), 148.8, 148.1, 129.5, 128.4, 127.7, 127.2, 115.8 (q, *J* = 287.8 Hz), 112.8, 109.3, 63.4, 55.9, 55.9, 40.9, 32.0.

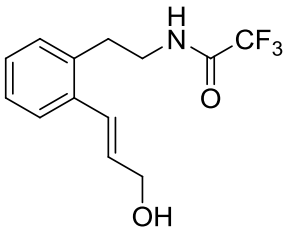



(*E*)-2,2,2-Trifluoro-*N*-(2-(6-(3-hydroxyprop-1-enyl)benzo[d][1,3]dioxol-5-yl)ethyl)acetamide **S4b**
Following the general procedure, 297 mg **S4b** (0.94 mmol, 78%) were isolated from the reaction of iodide **S2b** (464 mg, 1.2 mmol) after purification by column chromatography using ethyl acetate/pentane 2:1 as eluent.

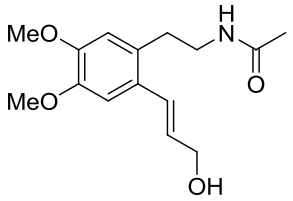
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.82 (dt, *J* = 15.6, 1.5 Hz, 1H), 6.61 (s, 1H), 6.46 (br s, 1H), 6.16 (dt, *J* = 15.6, 5.3 Hz, 1H), 5.95 (s, 2H), 4.33 (t, *J* = 5.3 Hz, 2H), 3.49 (q, *J* = 7.1 Hz, 2H), 2.89 (t, *J* = 7.1 Hz, 2H), 1.91 (t (br), *J* = 5.4 Hz, 1H).
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.5 (q, *J* = 37.0 Hz), 147.4, 147.2, 130.1, 130.0, 129.8, 128.7, 127.10, 109.6, 106.4, 101.1, 63.4, 40.9, 32.4.
$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -75.98.
HR-MS (ESI+, *m/z*): calculated for $C_{14}H_{14}F_3NO_4Na$ [M+$Na^+$]: 340.07671, found: 340.07650.




(*E*)-2,2,2-Trifluoro-*N*-(2-(3-hydroxyprop-1-enyl)-4-methylphenethyl)acetamide **S4c**
Following the general procedure, 104 mg **S4c** (0.36 mmol, 72%) were isolated from the reaction of iodide **S2c** (178 mg, 0.5 mmol) after purification by column chromatography using ethyl acetate/pentane 2:1 as eluent.
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.2 Hz, 1H), 7.07 – 6.99 (m, 2H), 6.88 (dt, *J* = 15.7, 1.2 Hz, 1H), 6.75 (s (br), 1H), 6.26 (dt, *J* = 15.7, 5.2 Hz, 1H), 4.34 (dd, *J* = 5.2, 1.2 Hz, 2H), 3.50 (q, *J* = 7.3 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.33 (s, 3H), 1.87 (s (br), 1H).
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.5 (q, *J* = 36.9 Hz), 137.0, 136.1, 131.9, 131.4, 129.8, 128.7, 127.4, 127.3, 63.4, 40.8, 32.2, 21.0. The $CF_3$ peaks could not be detected.
$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -75.99.




(*E*)-2,2,2-trifluoro-*N*-(2-(3-hydroxyprop-1-enyl)phenethyl)acetamide **S4d**
Following general procedure, heating the reaction mixture at 90 °C in this case, 108 mg **S4d** (0.4 mmol, 79%) were isolated from the reaction of bromide **S2d** (148 mg, 0.5 mmol) after purification by column chromatography using ethyl acetate/pentane 2:1 as eluent.
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.1, 2.3 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.13 (dd, *J* = 6.7, 2.2 Hz, 1H), 6.92 (dt, *J* = 15.7, 1.6 Hz, 1H), 6.90 (s (br), 1H), 6.26 (dt, *J* = 15.7, 5.2 Hz, 1H), 4.34 (dd, *J* = 5.2, 1.6 Hz, 2H), 3.51 (q, *J* = 7.3 Hz, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.61 (s (br), 1H).
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.5 (q, *J* = 37.1 Hz), 136.3, 134.9, 131.6, 129.9, 127.9, 127.5, 127.3, 126.7, 115.8, (q, *J* = 287.4 Hz), 63.3, 40.6, 32.6.
HR-MS (ESI+, *m/z*): calculated for $C_{13}H_{14}F_3NO_2Na$ [M+$Na^+$]: 296.08688, found: 296.08673.




(*E*)-*N*-(2-(3-hydroxyprop-1-enyl)-4,5-dimethoxyphenethyl)acetamide **S4e**

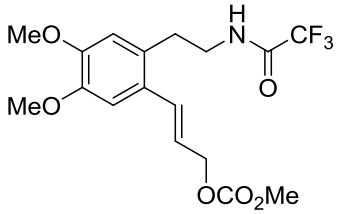
Following the general procedure, heating the reaction mixture at 80 °C in this case, 42 mg **S4e** (0.15 mmol, 30%) were isolated from the reaction of iodide **S2e** (139 mg, 0.4 mmol) after purification by column chromatography using ethyl acetate/methanol 10:1 as eluent.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 1H), 6.88 (dt, *J* = 15.7, 1.4 Hz, 1H), 6.62 (s, 1H), 6.17 (dt, *J* = 15.7, 5.4 Hz, 1H), 5.71 (s (br), 1H), 4.33 (dd, *J* = 5.3, 1.4 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.38 (q, *J* = 7.4 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.65 (s (br), 1H), 1.94 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.4, 148.6, 147.8, 129.3, 128.8, 128.6, 127.7, 112.8, 109.1, 63.5, 56.0, 55.9, 40.7, 33.0, 23.3.

**General procedure for the synthesis of allylic carbonates S5:**

To a solution of allyl alcohol **S4** (1 equiv.) and pyridine (3 equiv.) in $CH_2Cl_2$ (20 mL/mmol) methyl chloroformate (1.5 equiv.) was added dropwise at 0 °C. After 5 min. the solution was warmed to room temperature and was stirred for 1 h. Then, it was washed with aq. HCl (2N) (3 x 5 mL/mmol) and dried over $Na_2SO_4$. The corresponding product **S5** was obtained as a white solid after evaporation of the solvent.

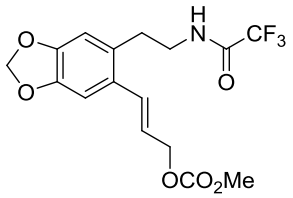



(*E*)-3-(4,5-Dimethoxy-2-(2-(2,2,2-trifluoroacetamido)ethyl)phenyl)allyl methyl carbonate **S5a** (**1**)

Following the general procedure, 280 mg of **S5a** (0.72 mmol, 90%) were isolated as a white solid from the reaction of allyl alcohol **S4a** (267 mg, 0.8 mmol).

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 1H), 6.89 (dt, *J* = 15.6, 1.0 Hz, 1H), 6.62 (s, 1H), 6.47 (s (br), 1H), 6.11 (dt, *J* = 15.6, 6.6 Hz, 1H), 4.80 (dd, *J* = 6.6, 1.0 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 3.80 (s, 3H), 3.51 (q, *J* = 6.8 Hz, 2H), 2.92 (t, *J* = 7.1 Hz, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.2 (q, *J* = 36.7 Hz), 155.7, 149.3, 148.1, 131.9, 128.3, 127.4, 123.0, 115.8 (q, *J* = 287.8 Hz), 112.7, 109.2, 68.6, 55.9, 55.8, 54.8, 40.8, 31.8.



(*E*)-Methyl 3-(6-(2-(2,2,2-trifluoroacetamido)ethyl)benzo[d][1,3]dioxol-5-yl)allyl carbonate **S5b**

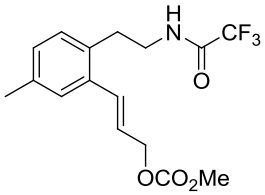
Following the general procedure, 258 mg of **S5b** (0.70 mmol, 92%) were isolated from the reaction of allyl alcohol **S4b** (240 mg, 0.76 mmol).

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.87 (dt, *J* = 15.6, 1.2 Hz, 1H), 6.62 (s, 1H), 6.59 (s (br), 1H), 6.05 (dt, *J* = 15.5, 6.5 Hz, 1H), 5.94 (s, 2H), 4.77 (dd, *J* = 6.5, 1.2 Hz, 2H), 3.79 (s, 3H), 3.47 (q, *J* = 7.1 Hz, 2H), 2.88 (t, *J* = 7.1 Hz, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.2 (q, *J* = 36.9 Hz), 155.7, 148.0, 147.1, 132.0, 129.6, 128.9, 123.5, 115.8 (q, *J* = 287.7 Hz), 109.7, 106.4, 101.3, 68.5, 54.8, 40.8, 32.2.

$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -76.01.

HR-MS (ESI+, *m/z*): calculated for $C_{16}H_{16}F_3NO_6Na$ [M+$Na^+$]: 398.08219, found: 398.08392.



(E)-Methyl 3-(5-methyl-2-(2-(2,2,2-trifluoroacetamido)ethyl)phenyl)allyl carbonate **S5c**

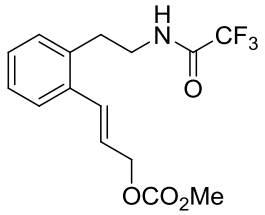
Following the general procedure, 114 mg of **S5c** (0.33 mmol, 95%) were isolated from the reaction of allyl alcohol **S4c** (101 mg, 0.35 mmol).

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 9.3 Hz, 1H), 7.12 – 6.98 (m, 2H), 6.93 (dt, *J* = 15.7, 1.3 Hz, 1H), 6.44 (s (br), 1H), 6.18 (dt, *J* = 15.6, 6.4 Hz, 1H), 4.80 (dd, *J* = 6.4, 1.3 Hz, 2H), 3.80 (s, 3H), 3.50 (q, *J* = 7.0 Hz, 2H), 2.93 (t, *J* = 7.0 Hz, 2H), 2.33 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.7 (q, *J* = 36.9 Hz), 155.3, 137.0, 135.1, 132.4, 132.2, 129.9, 129.3, 127.4, 125.0, 115.8 (q, *J* = 287.8 Hz), 68.5, 54.8, 40.7, 31.9, 21.0.

$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -76.02.

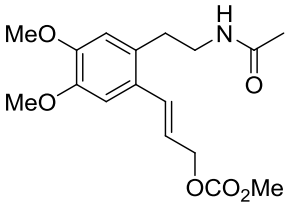
HR-MS (ESI+, *m/z*): calculated for $C_{16}H_{18}F_3NO_4Na$ [M+$Na^+$]: 368.10801, found: 368.10616.



(*E*)-methyl 3-(2-(2-(2,2,2-trifluoroacetamido)ethyl)phenyl)allyl carbonate **S5d**

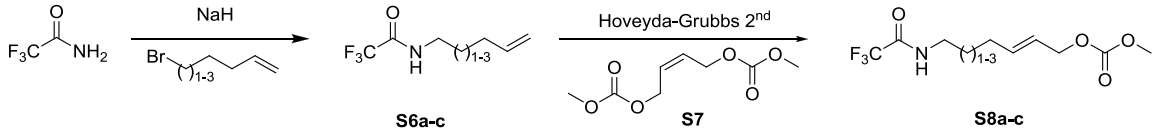
Following the general procedure, 126 mg of **S5d** (0.38 mmol, 95%) were isolated from the reaction of allyl alcohol **S4d** (108 mg, 0.4 mmol).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 5.7, 3.7 Hz, 1H), 7.31 – 7.18 (m, 2H), 7.14 (dd, *J* = 5.6, 3.6 Hz, 1H), 6.97 (dt, *J* = 15.7, 1.2 Hz, 1H), 6.73 (s (br), 1H), 6.18 (dt, *J* = 15.6, 6.4 Hz, 1H), 4.80 (dd, *J* = 6.4, 1.2 Hz, 2H), 3.78 (s, 3H), 3.51 (q, *J* = 7.3, 2H), 2.96 (t, *J* = 7.3, 2H).
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.3, (q, *J* = 37.0 Hz), 155.7, 135.4, 135.4, 132.1, 129.9, 128.5, 127.5, 126.8, 125.3, 115.8 (q, *J* = 287.7 Hz), 68.4, 54.8, 40.6, 32.4.
HR-MS (ESI+, *m/z*): calculated for $C_{15}H_{16}F_3NO_4Na$ [M+$Na^+$]: 354.09236, found: 354.09128.

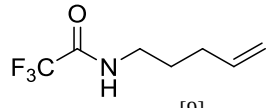



(*E*)-3-(2-(2-acetamidoethyl)-4,5-dimethoxyphenyl)allyl methyl carbonate **S5e** (**4**)
Following the general procedure, 29 mg of **S5e** (0.08 mmol, 86%) were isolated from the reaction of allyl alcohol **S4e** (28 mg, 0.1 mmol).
$^1$H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.64 (s, 1H), 6.10 (dt, *J* = 15.5, 6.6 Hz, 1H), 5.61 (s (br), 1H), 4.79 (d, *J* = 6.6 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.79 (s, 3H), 3.40 (q, *J* = 6.9 Hz, 2H), 2.84 (t, *J* = 6.9 Hz, 2H), 1.93 (s, 3H).
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.2, 155.7, 149.3, 147.9, 132.3, 129.6, 127.3, 122.4, 112.8, 109.0, 68.7, 55.97, 55.9, 54.8, 40.7, 32.5, 23.3.

## 2.2.) Starting Materials for Saturated Nitrogen Heterocycles synthesis

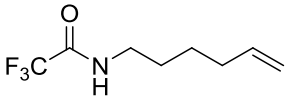



**General Procedure for the alkylation of 2,2,2-trifluoroacetamide to give S6**
2,2,2-trifluoroacetamide (1.0 eq.) was dissolved in DMF (Volume: 50 ml per 10 mmol) and added to a suspension of 1.05 eq. sodium hydride in DMF (Volume: 20 ml per 10 mmol) at 0 °C. After all gas evolution ceased, 1.05 eq. of the appropriate bromide was added and the reaction mixture was heated to 50 °C for 3 h. After the reaction showed full conversion (by TLC), 50 mL EtOAc was added and the reaction mixture was washed with water (80 mL per 10 mmol) and 2x with brine (2x 80 mL per 10 mmol). After drying over $MgSO_4$, all volatiles were removed under reduced pressure to give the desired alkyltrifluoroacetamides **S6a-c**. These products were used without further purification.



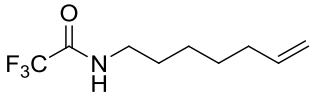
2,2,2-trifluoro-*N*-(pent-4-en-1-yl)acetamide **S6a**[9]
Following the general procedure for the alkylation of 2,2,2-trifluoroacetamide, 1.442 g of **S6a** (7.96 mmol, 99%) were isolated as a pale yellow oil from the reaction of 2,2,2-trifluoroacetamide (0.909 g, 8.04 mmol) with 5-bromopent-1-ene (1.00 ml, 8.44 mmol).

$^1$H NMR: (400 MHz, $CDCl_3$) δ = 7.23 (s (br), 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.14 – 4.84 (m, 2H), 3.39 – 3.22 (m, 2H), 2.19 – 1.95 (m, 2H), 1.78 – 1.58 (m, 3H).
$^{13}$C NMR: (100 MHz, $CDCl_3$) δ = 157.4 (q, *J* = 36.7), 137.0, 115.8 (q, *J* = 287.2 Hz), 115.5, 39.4, 30.7, 27.7.
$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -76.21.
HR-MS: calculated for $C_7H_{11}F_3NO$ [M+H$^+$]: 182.0787, found: 182.0784.



2,2,2-trifluoro-*N*-(hex-5-en-1-yl)acetamide **S6b**
Following the general procedure for the alkylation of 2,2,2-trifluoroacetamide, 1.352 g **S6b** (6,93 mmol, 98%) were isolated as a pale yellow oil from the reaction of 2,2,2-trifluoroacetamide (0.799 g, 7.07 mmol) with 6-bromo-1-hexene (1.00 ml, 7.42 mmol).

$^1$H NMR: (400 MHz, $CDCl_3$) δ = 7.30 (s (br) 1H), 5.83 – 5.59 (m, 1H), 5.11 – 4.70 (m, 2H), 3.34 – 3.22 (m, 2H), 2.09 – 2.00 (m, 2H), 1.63 – 1.48 (m, 2H), 1.47 – 1.31 (m, 2H).
$^{13}$C NMR: (101 MHz, $CDCl_3$) δ = 157.3 (q, *J* = 36.8 Hz), 137.9, 115.9 (q, *J* = 287.8 Hz), 114.8, 39.7, 33.0, 28.1, 25.8.
$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -76.10.
HR-MS: calculated for $C_8H_{13}F_3NO$ [M+H$^+$]: 196.0944, found: 196.1103.

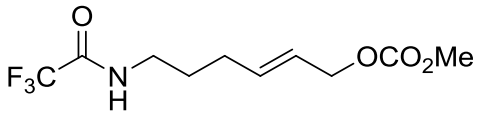


2,2,2-trifluoro-*N*-(hept-6-en-1-yl)acetamide **S6c**
Following the general procedure for the alkylation of 2,2,2-trifluoroacetamide, 1.294 g **S6c** (6.19 mmol, 99%) were isolated as a pale yellow oil from the reaction of 2,2,2-trifluoroacetamide (0.706 g, 6.25 mmol) with 7-bromohept-1-ene (1.00 ml, 6.56 mmol).

$^1$H NMR: (400 MHz, $CDCl_3$) δ = 6.68 (s (br), 1H), 5.92 – 5.61 (m, 1H), 5.08 – 4.84 (m, 2H), 3.40 – 3.27 (m, 2H), 2.12 – 1.97 (m, 2H), 1.67 – 1.51 (m, 2H), 1.48 – 1.29 (m, 4H).
$^{13}$C NMR: (101 MHz, $CDCl_3$) δ = 157.3 (q, *J* = 36.8 Hz), 138.4, 115.9 (q, *J* = 288.3 Hz), 114.6, 39.9, 33.4, 28.7, 28.3, 26.0.
$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -76.07.
HR-MS: calculated for $C_9H_{15}F_3NO$ [M+H$^+$]: 210.1100, found: 210.2215.

**General Procedure for the cross-metathesis of S6 with butendiyl dimethylcarbonate S7 to give allylic carbonates S8**

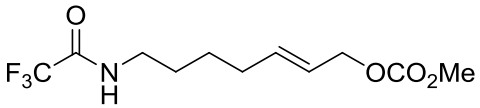
Trifluoroacetamides **S6a-c** (1.0 eq.) were dissolved under a $N_2$ atmosphere in degassed toluene (10 ml per 2 mmol), then 2.00 eq. (Z)-but-2-ene-1,4-diyl dimethyl dicarbonate **S7** were added and finally 5.0 mol% Hoveyda-Grubbs 2nd generation were added. The mixture was heated to 70 °C and stirred until TLC showed full conversion (2-6 hours). After cooling to ambient temperature, all volatiles were removed under reduced pressure and crude product was purified by column chromatography ($SiO_2$, Pentane/EtOAc) to give the pure compounds.




(E)-methyl (6-(2,2,2-trifluoroacetamido)hex-2-en-1-yl) carbonate **S8a**

Following the general procedure for the cross-metathesis of **S6** with butendiyl dimethylcarbonate **S7**, 1.00 g **S6a** (5.52 mmol) were reacted with 2.254 g **S7** (11.04 mmol) to give 1.233 g **S8a** (4.58 mmol, 83%) after column chromatography ($SiO_2$, pentane/EtOAc 10:1, $R_f$ = 0.20 in Pentane/EtOAc 10:1).

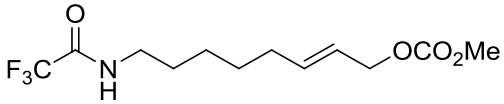
$^1$H NMR: (400 MHz, $CDCl_3$) δ = 6.75 (s (br), 1H), 5.76 (dd, *J* = 14.4, 7.6 Hz, 1H), 5.67 – 5.54 (m, 1H), 4.54 (d, *J* = 6.3, 2H), 3.75 (s, 3H), 3.34 (dd, *J* = 13.4, 6.7 Hz, 2H), 2.11 (dd, *J* = 14.2, 7.1 Hz, 2H), 1.77 – 1.57 (m, 2H).
$^{13}$C NMR: (101 MHz, $CDCl_3$) δ = 157.2 (q, *J* = 36.7 Hz), 155.6, 135.0, 124.6, 115.8 (q, *J* = 289.6 Hz), 68.1, 54.7, 39.3, 29.3, 27.8.
$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -76.02.
HR-MS: calculated for $C_{10}H_{14}F_3NO_4Na$ [M+$Na^+$]: 292.0767, found: 292.0762.




(E)-methyl (7-(2,2,2-trifluoroacetamido)hept-2-en-1-yl) carbonate **S8b**

Following the general procedure for the cross-metathesis of **S6** with butendiyl dimethylcarbonate **S7**, 0.500 g **S6b** (2.56 mmol) were reacted with 1.046 g **S7** (5.12 mmol) to give 0.573 g **S8a** (2.20 mmol, 79%) after column chromatography ($SiO_2$, pentane/EtOAc 10:1, $R_f$ = 0.18 in Pentane/EtOAc 10:1).

$^1$H NMR: (201 MHz, $CDCl_3$) δ = 7.22 (s (br), 1H), 5.87 – 5.35 (m, 2H), 4.47 (d, *J* = 6.2 Hz, 2H), 3.77 – 3.57 (m, 3H), 3.25 (dd, *J* = 13.0, 6.6 Hz, 3H), 2.15 – 1.91 (m, 2H), 1.76 – 1.24 (m, 4H).
$^{13}$C NMR: (50 MHz, $CDCl_3$) δ = 157.2 (q, *J* = 37.1 Hz), 155.4, 136.0, 123.7, 115.8 (q, *J* = 290.2 Hz), 68.2, 54.4, 39.5, 31.4, 28.0, 25.5.
$^{19}$F NMR: (189 MHz, $CDCl_3$) δ = -76.15.
HR-MS: calculated for $C_{11}H_{13}F_3NO_4Na$ [M+$Na^+$]: 306.0924, found: 306.0908.

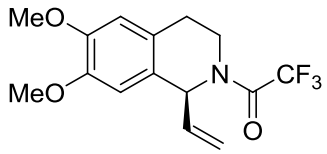


(E)-methyl (8-(2,2,2-trifluoroacetamido)oct-2-en-1-yl) carbonate **S8c** (**11**)
Following the general procedure for the cross-metathesis of **S6** with butendiyl dimethylcarbonate **S7**, 1.00 g **S6c** (4.78 mmol) were reacted with 1.952 g **S7** (9.56 mmol) to give 1.023 g **S8c** (3.44 mmol, 72%) after column chromatography ($SiO_2$, pentane/EtOAc 10:1, $R_f$ = 0.22 in Pentane/EtOAc 10:1).

$^1$H NMR: (201 MHz, $CDCl_3$) δ = 6.73 (s (br), 1H), 5.93 – 5.36 (m, 2H), 4.53 (d, *J* = 6.3 Hz, 2H), 3.74 (s, 3H), 3.31 (dd, *J* = 13.4, 6.7 Hz, 2H), 2.16 – 1.91 (m, 2H), 1.68 – 1.46 (m, 2H), 1.46 – 1.17 (m, 4H).
$^{13}$C NMR: (50 MHz, $CDCl_3$) δ = 157.2 (q, *J* = 36.4 Hz), 155.6, 136.6, 123.5, 115.9 (q, *J* = 288.5 Hz), 68.5, 54.6, 39.8, 31.9, 28.6, 28.1, 26.0.
$^{19}$F NMR: (189 MHz, $CDCl_3$) δ = -76.04.
HR-MS: calculated for $C_{12}H_{18}F_3NO_4Na$ [M+$Na^+$]: 320.1080, found: 320.1077.

## 3.) Asymmetric Allylic Amidation

**General Procedure for the Iridium-catalyzed asymmetric allylic amidation (Table 3)**
$[Ir(COD)Cl]_2$ (2.5 mol%) and 5.0 mol% **L2** were dissolved in dry THF (1.0 mL per 0.2 mmol) under a $N_2$ atmosphere. Then, 1.00 eq. DBU was added and the reaction mixture was heated at 50 °C for 30 min. Then, the solution was brought to the appropriate temperature and 1.0 eq. allylic carbonate **S5** or **S8** was added. The reaction mixture was stirred until TLC showed full conversion. All volatiles were removed under reduced pressure to yield the crude product as an orange oil. This was purified by column chromatography ($SiO_2$, Pentane/EtOAc) to yield the desired trifluoroacetamide.



(*S*)-1-(6,7-Dimethoxy-1-vinyl-3,4-dihydroisoquinolin-2(*1H*)-yl)-2,2,2-trifluoroethanone **2**
The title compound was prepared from **S5a** (**1**) (117 mg, 0.30 mmol) following the general procedure for the Ir-catalyzed asymmetric allylic amidation at room temperature. Purification by column chromatography ($SiO_2$, Pentane/EtOAc 3:1) afforded **2** (92 mg, 0.29 mmol, 95% *ee*, 97%) as a colourless oil as a mixture of two conformers in 3.6:1 ratio (determined by $^1$H NMR at 20 °C).
$^1$H NMR (400 MHz, $CDCl_3$) δ 6.62 (s, 1H, minor), 6.60 (s, 1H, major), 6.58 (s, 1H, major), 6.55 (s, 1H, minor), 6.00 – 5.91 (m, 2H major + 1H minor), 5.44 (d, *J* = 4.0 Hz, 1H minor), 5.30 (dd, *J* = 9.9, 0.8 Hz, 1H major), 5.29 (d, *J* = 10.0 Hz, 1H minor), 5.12

(dd, *J* = 15.5, 0.8 Hz, 1H major), 5.03 (d, *J* = 17.1 Hz, 1H minor), 4.51 – 4.46 (m, 1H minor), 4.03 – 3.98 (m, 1H major), 3.85 (s, 3H, minor), 3.84 (s, 3H, major), 3.84 (s, 3H, minor), 3.83 (s, 3H, major), 3.53 (ddd, *J* = 13.8, 12.1, 3.9 Hz, 1H major), 3.24 (td, *J* = 12.2, 4.2 Hz, 1H minor), 3.00 – 2.90 (m, 1H major + 1H minor), 2.76 – 2.68 (m, 1H major + 1H minor).

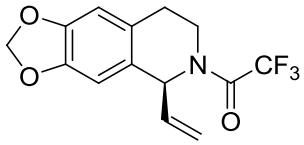
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.6 (q, *J* = 35.8 Hz) (major), 148.6 (minor), 148.3 (major), 147.8 (major), 147.7 (minor), 136.5 (minor), 135.6 (major), 126.0 (minor), 125.3 (major), 124.7 (major), 124.4 (minor), 118.6 (major), 118.5 (minor), 116.8 (q, *J* = 287.9 Hz), 111.4 (minor), 111.1 (major), 110.6 (major), 110.3 (minor), 57.9 (minor), 56.0 (minor), 56.0 (major), 55.9 (major), 55.5 (major), 40.0 (major), 37.7 (minor), 28.7 (major), 27.2 (minor).

$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -68.7 (minor), -69.4 (major).

HR-MS (APCI+, *m/z*): calculated for $C_{15}H_{17}F_3NO_3$ [M+H$^+$]: 316.1155, found: 316.1140.

$[\alpha]_D^{20}$ = + 168.3 (c = 0.85 in $CHCl_3$)

*ee* determination by chiral HPLC (Chiralpak OJ-H: n-heptane/2-propanol 90:10, 40 °C isotherm, 210 nm), retention times: 19.7 min (major), 24.7 min (minor).




(*S*)-2,2,2-Trifluoro-1-(5-vinyl-7,8-dihydro-[1,3]dioxolo[4,5-*g*]isoquinolin-6(*5H*)-yl)ethanone **5**

The title compound was prepared from **S5b** (75 mg, 0.20 mmol) following the general procedure at room temperature. Purification by column chromatography ($SiO_2$, Pentane/$Et_2O$ 10:1) afforded **5** (54 mg, 0.18 mmol, 94% *ee*, 89%) as a colourless oil as a mixture of two conformers in 3.5:1 ratio (determined by $^1$H NMR at 20 °C).

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.61 (s, 1H, minor), 6.58 (s, 2H, major), 6.56 (s, 1H, minor), 6.02 – 5.88 (m, 4H major + 3H minor), 5.40 (d, *J* = 4.2 Hz, 1H minor), 5.30 (dd, *J* = 9.9, 1.0 Hz, 1H major), 5.29 (d, *J* = 10.1 Hz, 1H minor), 5.12 (dd, *J* = 15.5, 1.0 Hz, 1H major), 5.05 (d, *J* = 17.2 Hz, 1H minor), 4.46 – 4.39 (m, 1H minor), 4.02 – 3.94 (m, 1H major), 3.54 (ddd, *J* = 14.0, 11.6, 3.9 Hz, 1H major), 3.24 (td, *J* = 11.5, 4.7 Hz, 1H minor), 2.97 – 2.87 (m, 1H major + 1H minor), 2.75 – 2.68 (m, 1H major + 1H minor).

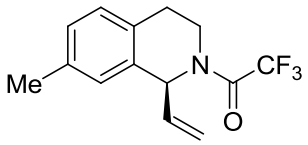
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.8 (q, *J* = 35.8 Hz) (major), 147.3 (minor), 147.0 (major), 146.5 (major), 146.4 (minor), 136.4 (minor), 135.5 (major), 127.3 (minor), 126.5 (major), 125.8 (major), 125.6 (minor), 118.5 (major), 118.4 (minor), 116.5 (q, *J* = 288.0 Hz) (major), 108.6 (minor), 108.3 (major), 107.8 (major), 107.4 (minor), 101.2 (minor), 101.1 (major), 58.1 (minor), 55.9 (major), 40.0 (major), 37.9 (minor), 29.1 (major), 27.6 (minor).

$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -68.7 (minor), -69.4 (major).

HR-MS (APCI+, *m/z*): calculated for $C_{14}H_{13}F_3NO_3$ [M+H$^+$]: 300.08420, found: 300.08388.

$[\alpha]_D^{20}$ = + 153.2 (c = 1.0 in $CHCl_3$)

*ee* determination by chiral HPLC (Chiralpak AD-H: n-heptane/2-propanol 98:2, 40 °C isotherm, 210 nm), retention times: 23.4 min (minor), 24.7 min (major).




(*S*)-2,2,2-Trifluoro-1-(7-methyl-1-vinyl-3,4-dihydroisoquinolin-2(*1H*)-yl)ethanone **6**

The title compound was prepared from **S5c** (34 mg, 0.15 mmol) following the general procedure at room temperature. Purification by column chromatography ($SiO_2$, Pentane/$Et_2O$ 20:1) afforded **6** (25 mg, 0.14 mmol, 91% *ee*, 92%) as a colourless oil as a mixture of two conformers in 3.1:1 ratio (determined by $^1$H NMR at 20 °C).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.2 Hz, 1H major +1H minor), 7.04 (s, 1H, major + 1H minor), 6.95 (d, *J* = 8.2 Hz, 1H major +1H minor), 6.06 – 5.93 (m, 2H major + 1H minor), 5.50 (d, *J* = 4.0 Hz, 1H minor), 5.32 – 5.28 (m, 1H major +1H minor), 5.12 (dd, *J* = 16.3, 0.7 Hz, 1H major), 5.04 (d, *J* = 17.0 Hz, 1H minor), 4.49 – 4.44 (m, 1H minor), 4.05 – 4.00 (m, 1H major), 3.58 (ddd, *J* = 14.0, 11.8, 4.0 Hz, 1H major), 3.24 (td, *J* = 12.4, 4.7 Hz, 1H minor), 3.03 – 2.93 (m, 1H major + 1H minor), 2.84 – 2.76 (m, 1H major + 1H minor), 2.33 (s, 3H minor), 2.33 (s, 3H major).

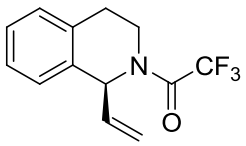
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.6 (q, *J* = 36.0 Hz) (major), 136.6 (minor), 136.3 (major), 136.1 (minor), 135.6 (major), 132.8 (major), 132.6 (minor), 130.1 (major), 130.0 (minor), 128.9 (minor), 128.6 (major), 128.5 (major), 128.2 (major), 128.1 (minor), 118.2 (major), 118.1 (minor), 116.5 (q, *J* = 287.7 Hz) (major), 58.3 (minor), 56.0 (major), 40.3 (major), 38.22 (minor), 28.7 (major), 27.2 (minor), 21.0 (major), 20.99 (minor).

$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -68.7 (minor), -69.4 (major).

HR-MS (ESI+, *m/z*): calculated for $C_{14}H_{15}F_3NO$ [$M+H^+$]: 270.11003, found: 270.10880.

$[\alpha]_D^{20}$ = + 152.4 (c = 1.0 in $CHCl_3$)

*ee* determination by chiral HPLC (Chiralpak OJ-H: n-heptane/2-propanol 99:1, 40 °C isotherm, 210 nm), retention times: 13.3 min (minor), 15.2 min (major).



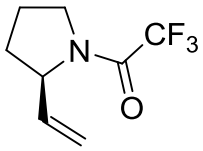

(*S*)-2,2,2-Trifluoro-1-(1-vinyl-3,4-dihydroisoquinolin-2(*1H*)-yl)ethanone **7**

The title compound was prepared from **S5d** (33 mg, 0.10 mmol) following the general procedure at room temperature. Purification by column chromatography ($SiO_2$, Pentane/$Et_2O$ 15:1) afforded **7** (20 mg, 0.08 mmol, 94% *ee*, 78%) as a colourless oil as a mixture of two conformers in 3.4:1 ratio (determined by $^1$H NMR at 20 °C).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.11 (m, 4H major + 4H minor), 6.05 – 5.93 (m, 2H major + 1H minor), 5.55 (d, *J* = 3.8 Hz, 1H minor), 5.31 (dd, *J* = 9.8, 1.1 Hz, 1H major), 5.30 (d, *J* = 10.2 Hz, 1H minor), 5.12 (dd, *J* = 16.5, 1.1 Hz, 1H major), 5.05 (d, *J* = 17.1 Hz, 1H minor), 4.51 – 4.45 (m, 1H minor), 4.08 – 4.00 (m, 1H major), 3.60 (td, *J* = 12.0, 4.0 Hz, 1H major), 3.33 (td, *J* = 12.0, 4.5 Hz, 1H minor), 3.08 – 2.98 (m, 1H major + 1H minor), 2.88 – 2.80 (m, 1H major + 1H minor).

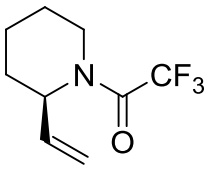
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.6 (q, *J* = 36.0 Hz) (major), 136.6 (minor), 135.6 (major), 133.9 (minor), 133.6 (minor), 133.2 (major), 133.0 (major), 129.1 (minor), 128.8

(major), 128.2 (major), 127.7 (minor), 127.7 (minor), 127.3 (major), 126.6 (major), 126.5 (minor), 118.3 (major), 118.3 (minor), 116.5 (q, *J* = 287.9 Hz) (major), 58.2 (minor), 55.9 (major), 40.1 (major), 38.0 (minor), 29.1 (major), 27.6 (minor).
$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -68.7 (minor), -69.4 (major).
HR-MS (ESI+, *m/z*): calculated for $C_{13}H_{13}F_3NO$ [M+H$^+$]: 256.09438, found: 256.09406.
$[\alpha]_D^{20}$ = + 186.8 (c = 1.0 in $CHCl_3$)
*ee* determination by chiral HPLC (Chiralpak OJ-H: n-heptane/2-propanol 98:2, 40 °C isotherm, 220 nm), retention times: 12.1 min (minor), 14.4 min (major).




(R)-2,2,2-trifluoro-1-(2-vinylpyrrolidin-1-yl)ethanone (**8**)
The title compound was prepared from **S8a** (0.100 g, 0.371 mmol) following the general procedure for the Ir-catalyzed asymmetric allylic amidation at 50 °C. Purification by column chromatography ($SiO_2$, Pentane/EtOAc 10:1, $R_f$ = 0.75 in Pentane/EtOAc 10:1) afforded **8** (0.040 g, 0.207 mmol, 96% *ee*, 56%) as a colourless oil.

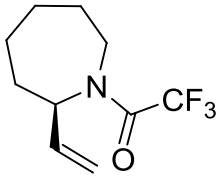
Product was isolated as a mixture of 2 conformers. (ratio 1 : 2.5)
$^1$H NMR: (201 MHz, $CDCl_3$) δ = 5.92 – 5.53 (m, 1H), 5.28 – 4.97 (m, 2H), 4.67 (d, *J* = 4.9 Hz, 1H), 3.78 – 3.46 (m, 2H), 2.16 – 1.70 (m, 4H).
$^{13}$C NMR: (101 MHz, $CDCl_3$) δ = 155.4 (q, *J* = 37.1 Hz), 136.8 (minor), 135.3 (major), 116.3 (q, *J* = 287.9 Hz, major), 116.2 (q, *J* = 286.6 Hz, minor), 115.4 (major), 115.1 (minor), 60.4 (major), 59.8 (minor), 47.3 (minor), 46.6 (major), 32.3 (minor), 29.8 (major), 23.8 (major), 20.1 (minor).
$^{19}$F NMR: (189 MHz, $CDCl_3$) δ = -70.94 (minor), -72.71 (major).
HR-MS: calculated for $C_8H_{11}F_3NO$ [M+H$^+$]: 194.0787, found: 194.0790.
$[\alpha]_D^{20}$ = 44.6 (c = 1.0 in $CHCl_3$)
*ee* determination by chiral HPLC (Chiralpak AD-H: n-heptane/2-propanol 98:2, 40 °C isotherm, 210 nm), retention times: 10.5 min (major), 11.5 min (minor).




(R)-2,2,2-trifluoro-1-(2-vinylpiperidin-1-yl)ethanone (**9**)
The title compound was prepared from **S8b** (0.060 g, 0.212 mmol) following the general procedure for the Ir-catalyzed asymmetric allylic amidation at 50 °C. Purification by column chromatography ($SiO_2$, Pentane/EtOAc 20:1, $R_f$ = 0.90 in Pentane/EtOAc 10:1) afforded **9** (0.030 g, 0.144 mmol, 88% *ee*, 68%) as a colourless oil.

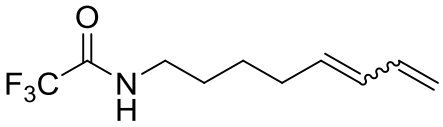
Product was isolated as a mixture of 2 conformers (ratio 1:1.7).

$^{1}$H NMR: (400 MHz, $CDCl_3$) δ = 5.95 – 5.65 (m, 1H), 5.31 (t, *J* = 11.5 Hz, 1H), 5.26 (s (br), 1H major), 5.15 (t, *J* = 16.4 Hz, 1H), 4.68 (s, 1H, minor), 4.39 (d, *J* = 12.7 Hz, 1H, minor), 3.80 (d, *J* = 13.3 Hz, 1H, major), 3.24 (t, *J* = 13.3 Hz, 1H, major), 2.91 (t, *J* = 13.0 Hz, 1H, minor), 1.90 (d, *J* = 13.2 Hz, 1H), 1.81 – 1.60 (m, 4H), 1.58 – 1.41 (m, 1H).
$^{13}$C NMR: (50 MHz, $CDCl_3$) δ = 156.8 (q, *J* = 36.6 Hz), 135.2 (minor), 134.6 (major), 117.8 (minor), 117.5 (major), 116.7 (q, *J* = 186.9 Hz), 54.8 (minor), 51.9 (major), 42.0 (minor), 39.2 (major), 29.6 (minor), 28.3 (major), 26.0 (major), 25.3 (minor), 19.3
$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -68.75 (minor), -68.79 (major).
HR-MS: calculated for $C_9H_{12}F_3NONa$ [M+$Na^+$]: 230.0763, found: 230.0752.
$[\alpha]_D^{20}$ = 55.6 (c = 1.2 in $CHCl_3$)
*ee* determination by chiral HPLC (Chiralpak OB-H: n-heptane/2-propanol 99.9:0.1, 40 °C isotherm, 230 nm), retention times: 13.5 min (minor), 15.2 min (major).




(R)-2,2,2-trifluoro-1-(2-vinylazepan-1-yl)ethanone (**10**)
The title compound was prepared from **S8c** (**11**) (0.100 g, 0.336 mmol) following the general procedure for the Ir-catalyzed asymmetric allylic amidation at 50 °C. Purification by column chromatography ($SiO_2$, Pentane/EtOAc 10:1, $R_f$ = 0.90 in Pentane/EtOAc 10:1) afforded **10** (0.019 g, 0.086 mmol, 92% *ee*, 25%) as a colourless oil.

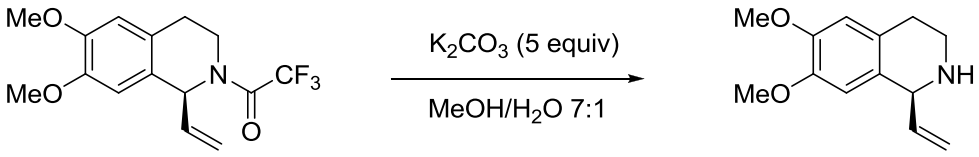
Product was isolated as a mixture of 2 conformers. (ratio 2:3)
$^{1}$H NMR: (400 MHz, $CDCl_3$) δ = 5.87 – 5.64 (m, 1H), 5.13 (dd, *J* = 19.5, 10.6 Hz, 1H), 5.05 (d, *J* = 17.3 Hz, 1H), 4.92 – 4.81 (m, 1H, minor), 4.45 (s (br), 1H, major), 4.06 (d, *J* = 13.6 Hz, 1H, major), 3.81 (d, *J* = 15.0 Hz, 1H, minor), 3.19 – 3.04 (m, 1H, minor), 2.82 (t, *J* = 12.7 Hz, 1H, major), 2.20 (ddd, *J* = 23.2, 15.0, 7.2 Hz, 1H), 1.98 – 1.79 (m, 2H), 1.69 - 1.46 (m, 3H), 1.30 (tt, *J* = 17.3, 8.7 Hz, 2H).
$^{13}$C NMR: (101 MHz, $CDCl_3$) δ = 136.7 (major), 135.6 (minor), 114.8 (major), 114.6 (minor), 58.3 (minor), 57.9 (major), 43.1 (minor), 42.9 (major), 33.7 (major), 32.3 (minor), 30.7 (minor), 29.6 (major), 28.9 (minor), 26.6 (major), 24.8 (minor), 23.9 (major). The $COCF_3$ peaks could not be detected.
$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -68.31 (major), -68.72 (minor).
HR-MS: calculated for $C_{10}H_{15}F_3NO$ [M+$H^+$]: 222.1100, found: 222.1103.
$[\alpha]_D^{20}$ = 76.8 (c = 1.0 in $CHCl_3$)
*ee* determination by chiral HPLC (Chiralpak AS-H: n-heptane/2-propanol 99:1, 40 °C isotherm, 220 nm), retention times: 9.4 min (minor), 10.0 min (major).



2,2,2-trifluoro-*N*-(octa-5,7-dienyl)acetamide (**12**)
The title compound was prepared from **S8c** (**11**) (0.100 g, 0.336 mmol) following the general procedure for the Ir-catalyzed asymmetric allylic amidation at 50 °C. Purification by column chromatography ($SiO_2$, Pentane/EtOAc 10:1, $R_f$ = 0.70 in Pentane/EtOAc 10:1) afforded **10** (0.019 g, 0.086 mmol, 92% *ee*, 25%) as a colourless oil.

Product was isolated as a mixture of 2 isomers. (ratio 3:2)
$^1$H NMR: (400 MHz, $CDCl_3$) δ = 6.60 (dt, *J* = 16.9, 10.6 Hz, 1H, major), 6.41 (s (br), 1H), 6.36 – 6.23 (m, 1H, minor), 6.13 – 5.97 (m, 1H), 5.78 – 5.59 (m, 1H, minor), 5.50 – 5.34 (m, 1H, major), 5.20 (d, *J* = 16.9 Hz, 1H, major), 5.16 – 5.04 (m, 1H), 4.98 (d, *J* = 10.1 Hz, 1H, minor), 3.36 (dd, *J* = 13.4, 6.7 Hz, 2H), 2.23 (q, *J* = 7.3 Hz, 2H, major), 2.12 (dd, *J* = 14.3, 7.1 Hz, 2H, minor), 1.69 – 1.53 (m, 2H), 1.51 – 1.38 (m, 2H).
$^{13}$C NMR: (101 MHz, $CDCl_3$) δ = 157.2 (q, *J* = 39.0 Hz), 137.0, 134.0, 131.9, 131.7, 131.4, 123.0, 117.5, 115.8 (q, *J* = 288.0 Hz), 115.3, 39.8, 31.9, 29.7, 28.41, 27.0, 26.5, 26.1.
$^{19}$F NMR: (376 MHz, $CDCl_3$) δ = -76.00.
HR-MS: calculated for $C_{10}H_{15}F_3NO$ [M+H$^+$]: 222.1103, found: 222.1100.

## 4.) Deprotection of Trifluoroacetamides



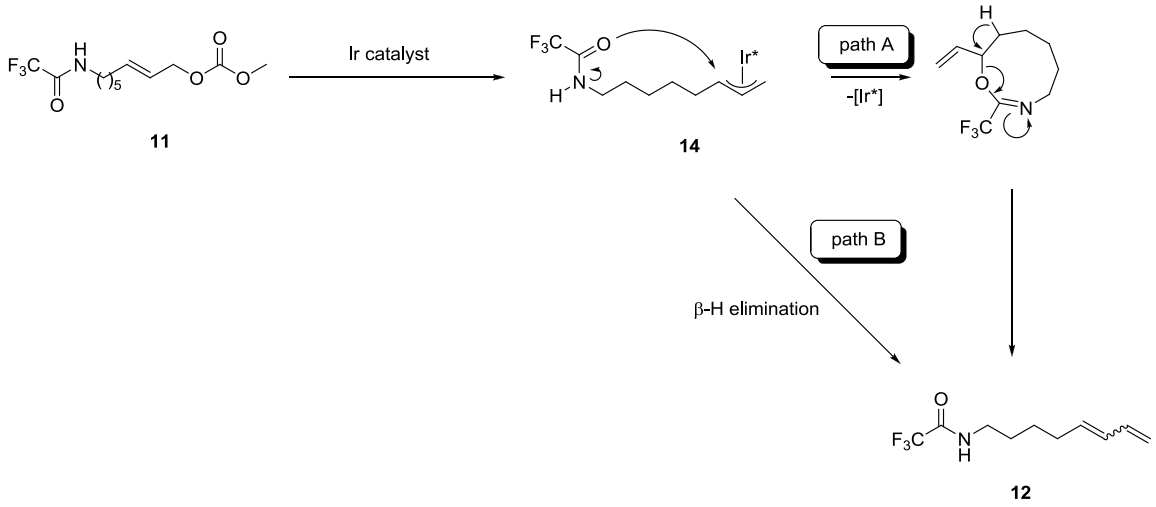

**2** **13**

**Procedure for the deprotection of trifluoroamide 2:**
Trifluoroacetamide **2** (46 mg, 0.15 mmol) was dissolved in a mixture of MeOH/water (7 mL/1 mL) at room temperature. $K_2CO_3$ was added to the solution and the resulting mixture was stirred during 16 h. Then, MeOH was removed under vacuum, water was added (10 mL) and the aqueous solution was extracted with AcOEt (3 x 5 mL). The combined organic layer was dried with $Na_2SO_4$ and the solvent was removed to afford amine **13** as a white solid (32 mg, 96%, 97% ee).
$^1$H NMR (300 MHz, $CDCl_3$) δ 6.58 (s, 1H), 6.57 (s, 1H), 5.93 (ddd, *J* = 17.4 Hz, 10.0, 7.8 Hz, 1H), 5.24 (d, *J* = 17.4 Hz, 1H), 5.23 (d, *J* = 10.0 Hz, 1H), 4.40 (d, *J* = 7.8 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.27 – 3.19 (m, 1H), 3.06 – 2.97 (m, 1H), 2.86 – 2.77 (m, 1H), 2.67 (dt, *J* = 16.1, 4.8 Hz, 1H), 2.13 (s (br), 1H).
$^{13}$C NMR (75 MHz, $CDCl_3$) δ 147.9, 147.3, 140.8, 128.7, 127.1, 117.5, 111.8, 110.5, 60.2, 56.2, 55.9, 41.9, 29.3.
HR-MS (ESI+, *m/z*): calculated for $C_{13}H_{18}NO_2$ [M+H$^+$]: 220.13321, found: 220.13251.
$[\alpha]_D^{20}$ = + 76.0 (c = 0.5, $CHCl_3$)

*ee* determination by chiral HPLC (Chiralpak OJ-H: n-heptane/2-propanol 98:2, 40 °C isotherm, 210 nm), retention times: 30.4 min (major), 38.7 min (minor).

## 5.) Discussion of the possible mechanisms for the formation of diene 12 from allylic carbonate 11 (Addition to Scheme 2)

In the following, a putative mechanism for this reaction is presented. After formation of the allyl-Ir-complex from allylic carbonate **11**, the oxygen atom of the trifluoroacetate could act as a nucleophile for the allylic substitution (path A); a reaction related to recent observations made in the Ir-catalyzed asymmetric allylic substitution with thiocarbamates,[10] resulting in a 9-membered heterocycle, which can undergo elimination to form the linear diene **12**.
Alternatively, Ir-complex **14** could unergo β-hydride elimination to form **12** directly (path B). This could indicate a relatively long-lived intermediate **14**, which could be explained by the sterically unfavoured formation of a seven-membered ring.




## 6.) References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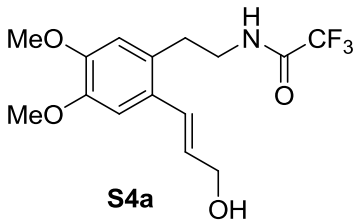
## 7.) NMR spectra and HPLC traces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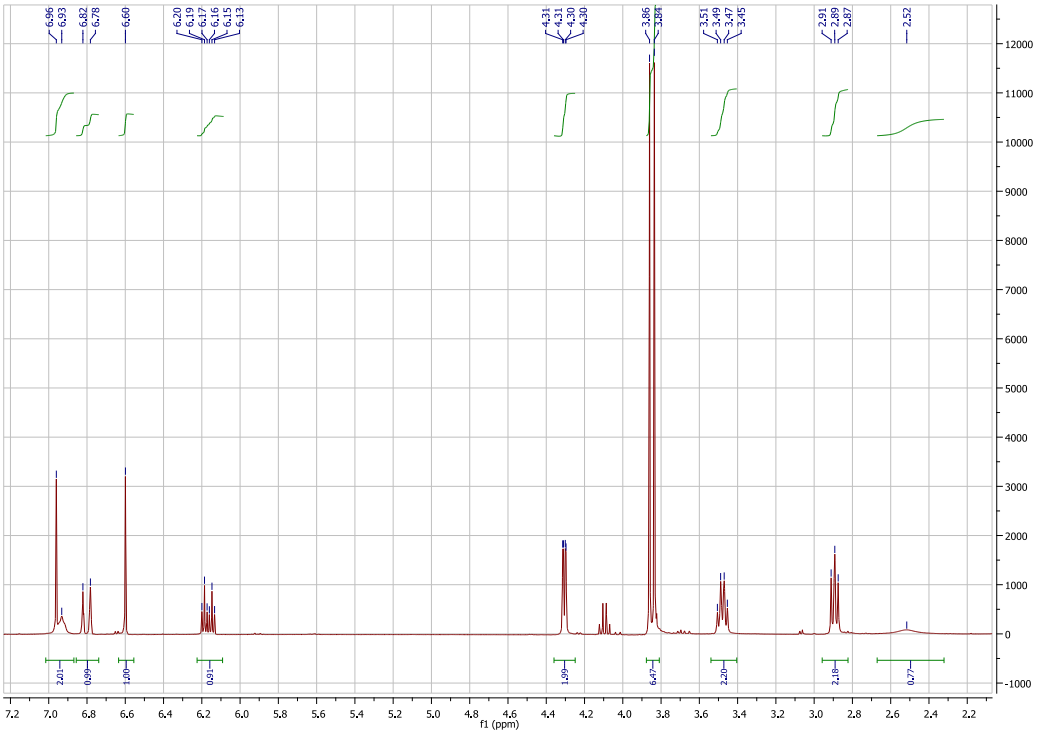
MeO
H
N
CF3
O
OH

**S4a**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6.17
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6.15
6.13
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4.31
4.30
4.30
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3.51
3.49
3.47
3.45
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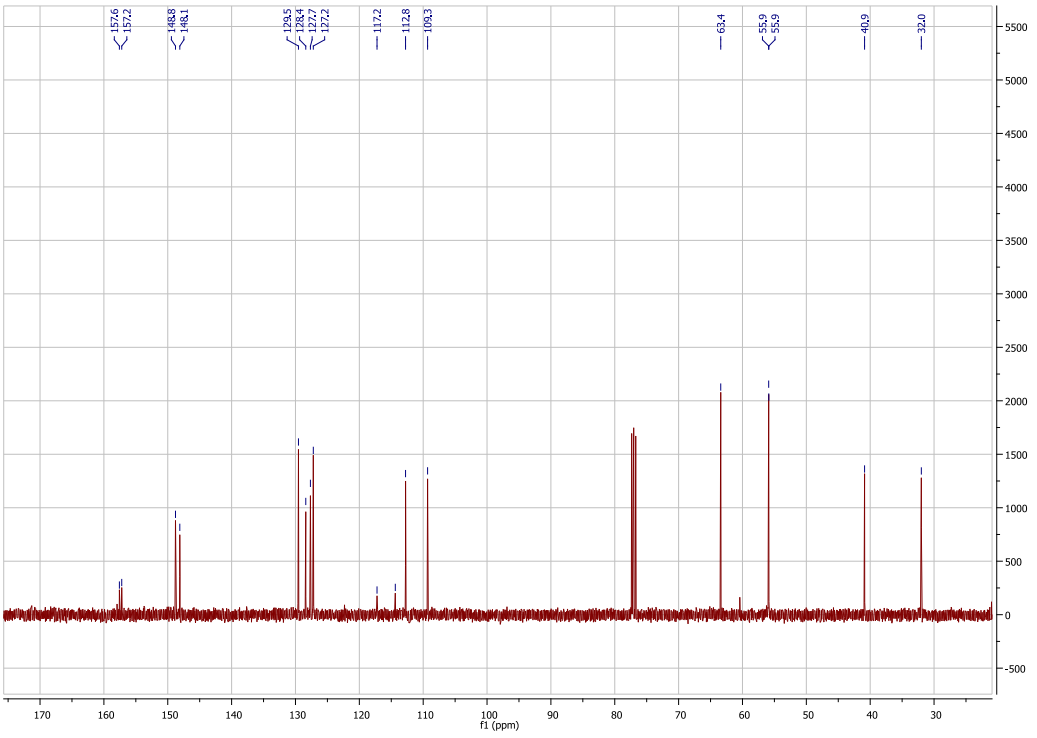
2.89
2.87
2.52
f1 (ppm)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157.2
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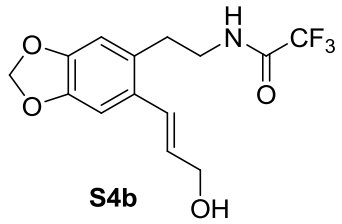
148.1
129.5
128.4
127.7
127.2
117.2
112.8
109.3
63.4
55.9
55.9
40.9
32.0
f1 (ppm)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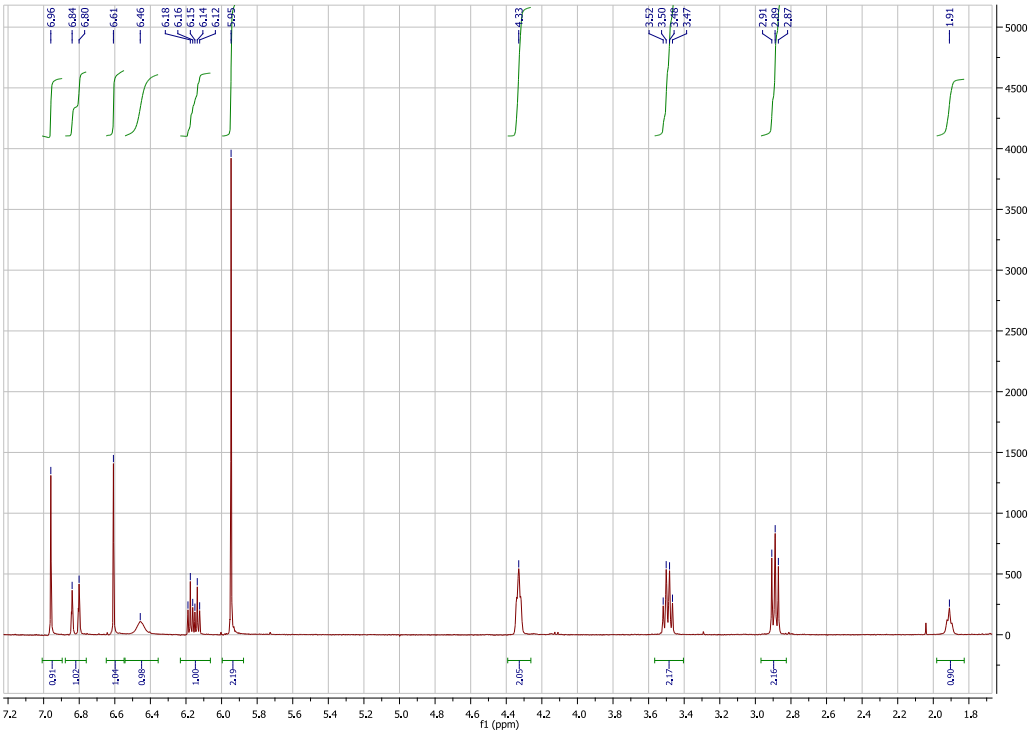
N
CF3
O
O
O
OH

**S4b**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6.61
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6.18
6.16
6.15
6.14
6.12
5.95
4.33
3.52
3.50
3.49
3.47
2.91
2.89
2.87
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0.91
1.02
1.04
0.98
1.00
2.19
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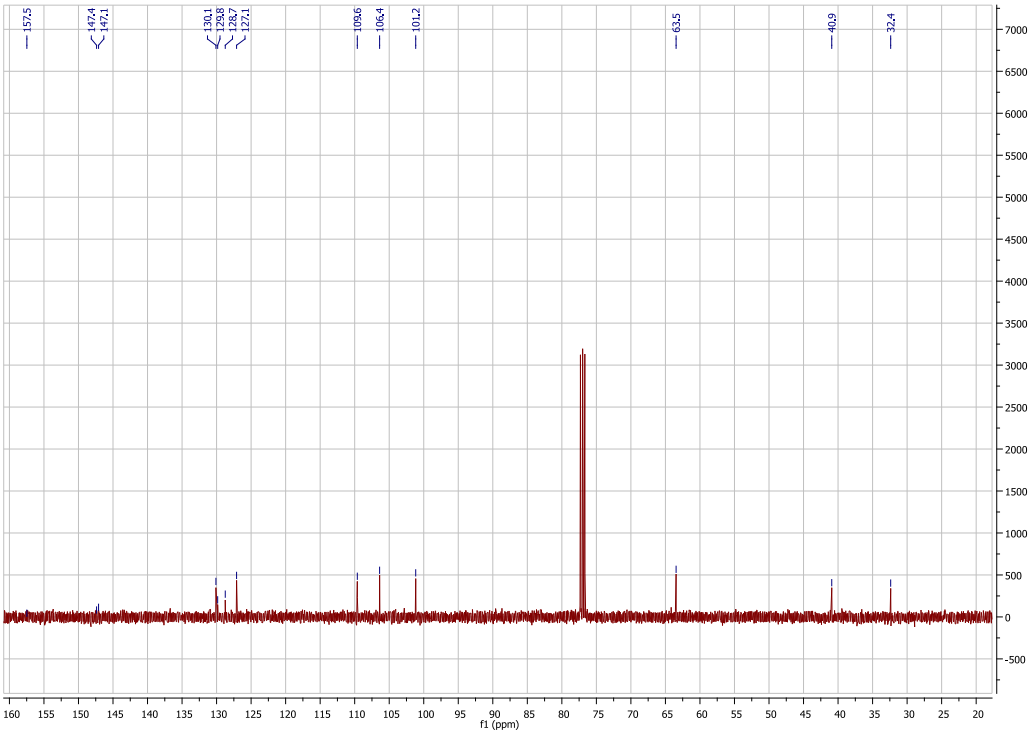
0.90
f1 (ppm)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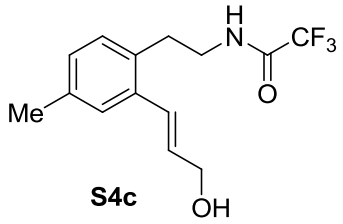
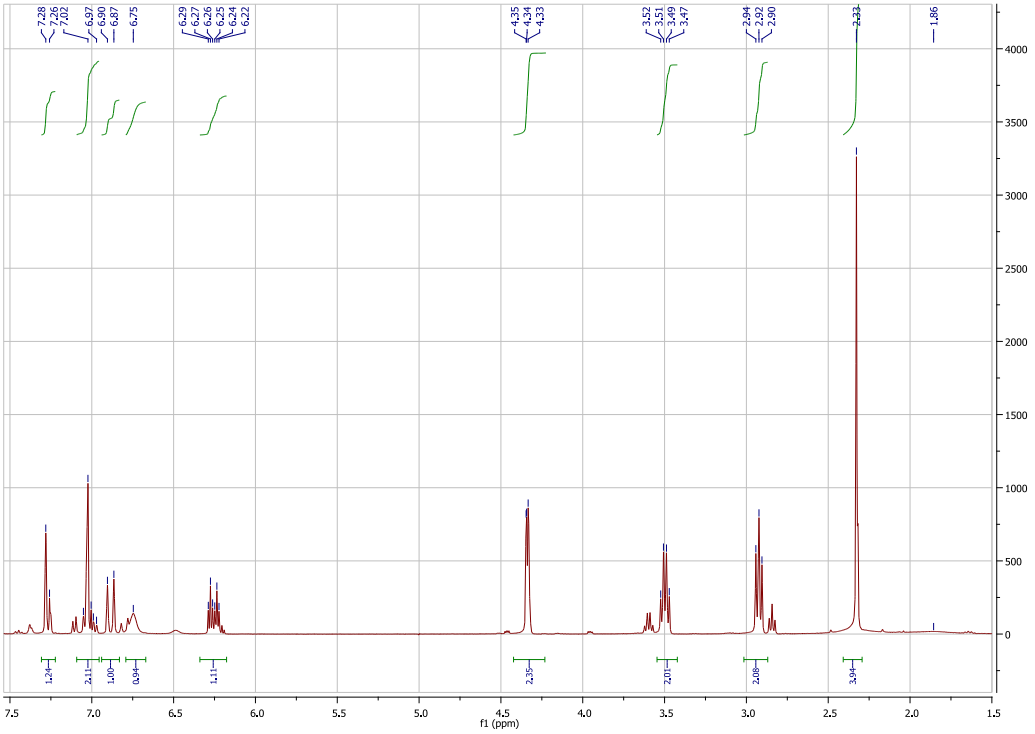
128.7
127.1
109.6
106.4
101.2
63.5
40.9
32.4
f1 (ppm)


H
N
CF3
O
Me
OH

**S4c**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6.26
6.25
6.24
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4.34
4.33
3.52
3.51
3.49
3.47
2.94
2.92
2.90
2.33
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2.11
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0.94
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2.01
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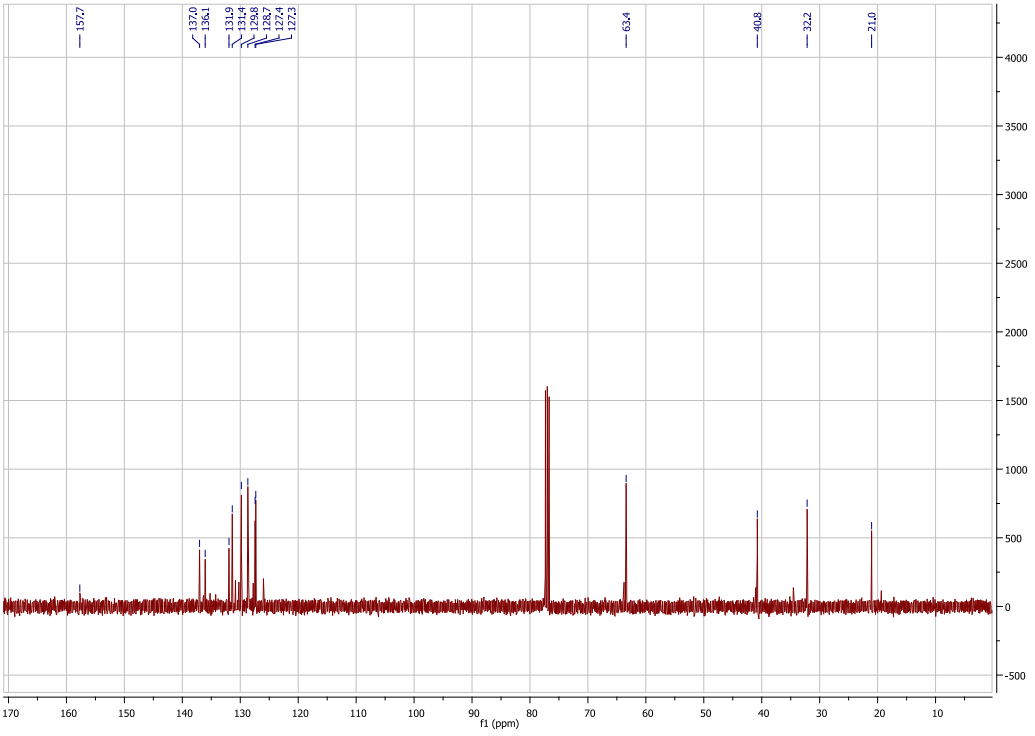
f1 (ppm)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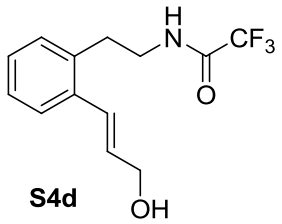
f1 (ppm)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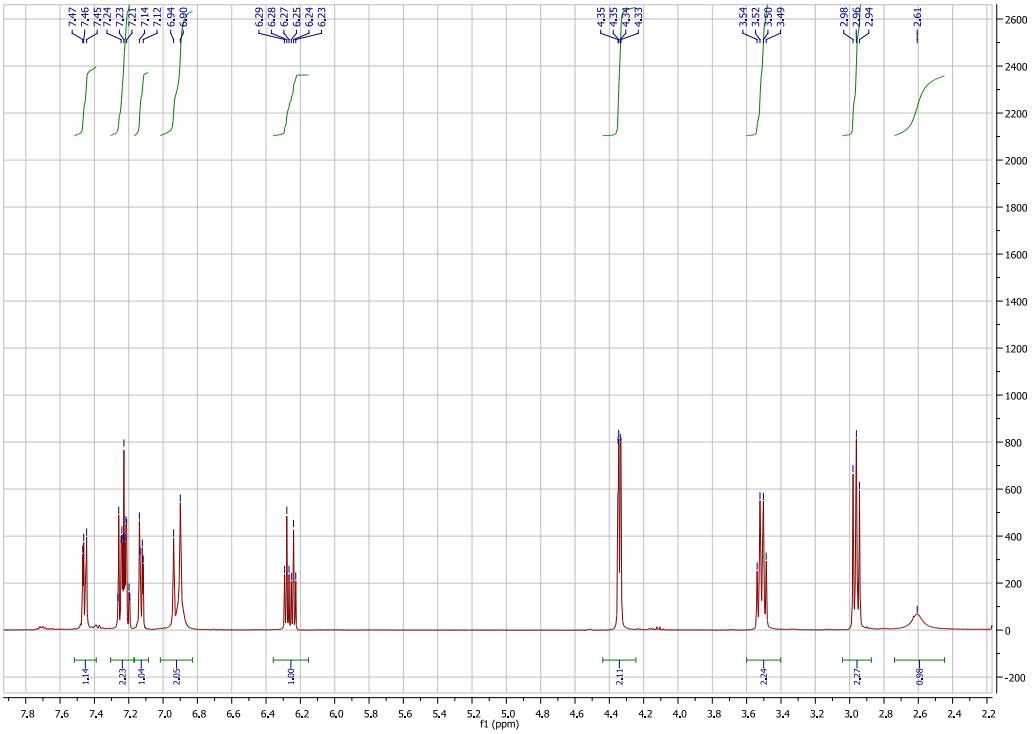
N
CF3
O
OH

**S4d**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7.12
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6.29
6.28
6.27
6.25
6.24
6.23
4.35
4.35
4.34
4.33
3.54
3.52
3.50
3.49
2.98
2.96
2.94
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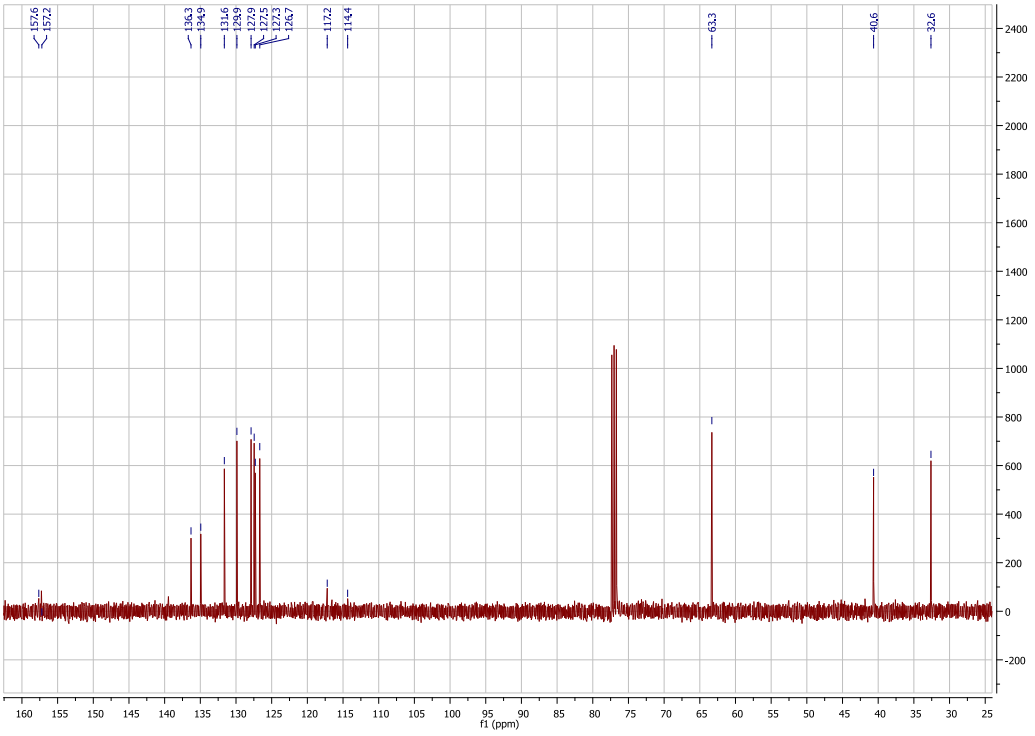
0.88
f1 (ppm)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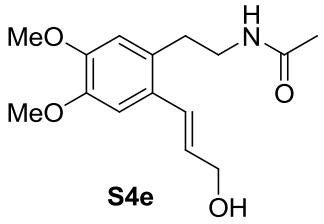
32.6
f1 (ppm)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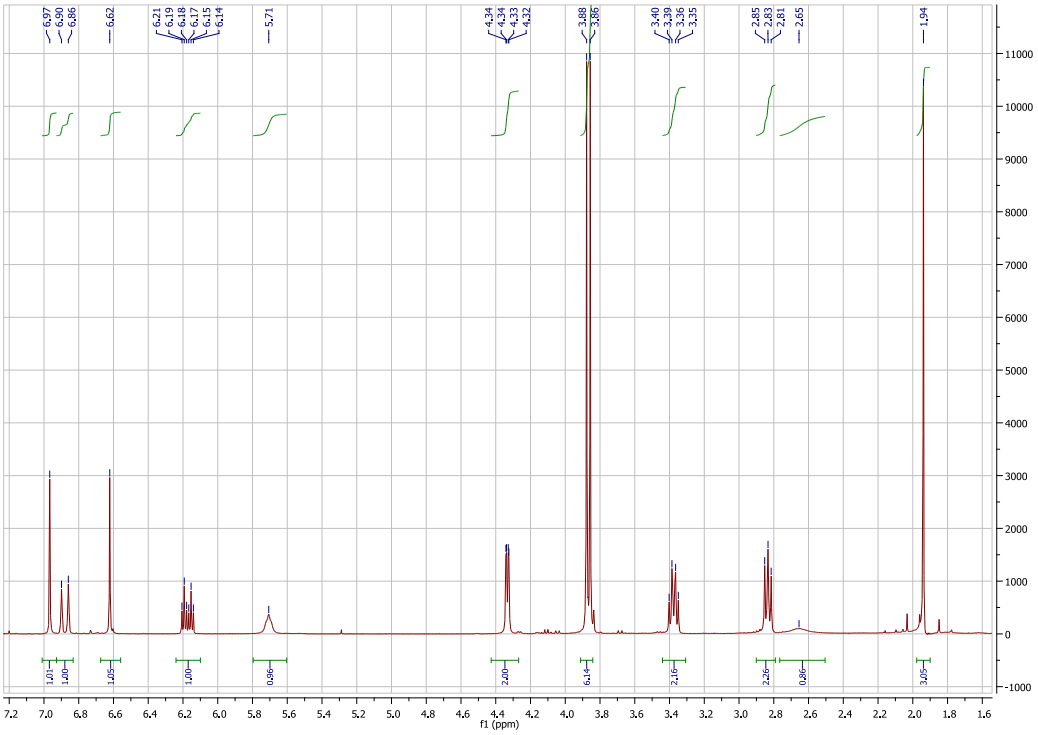
MeO
H
N
O
OH

**S4e**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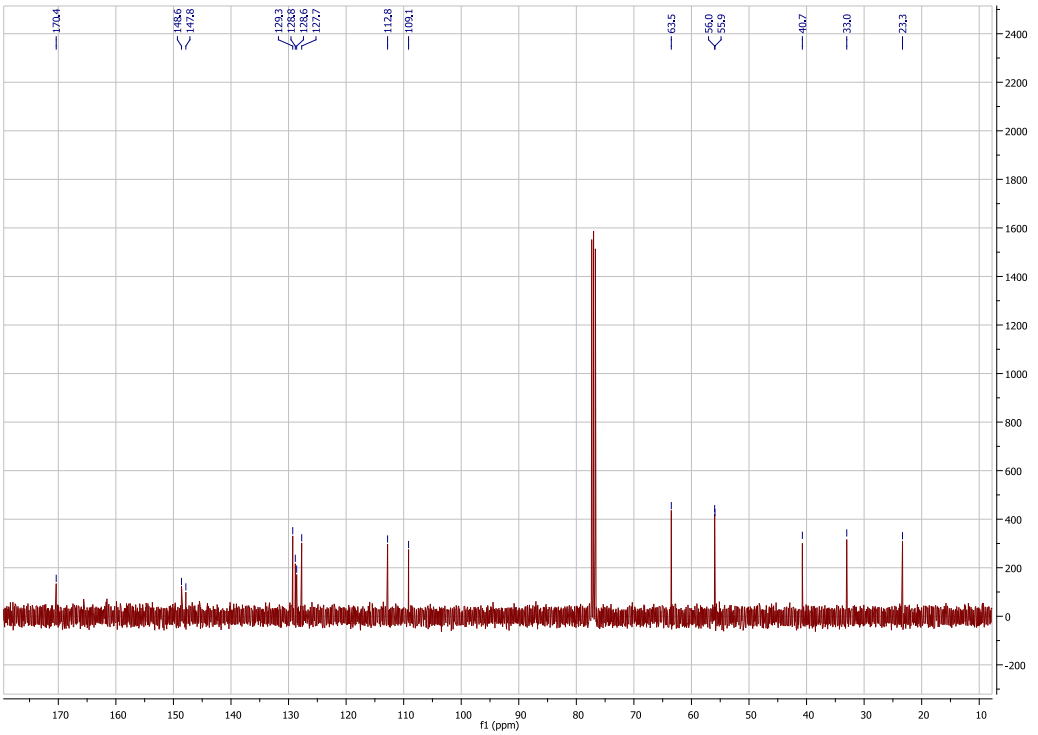
f1 (ppm)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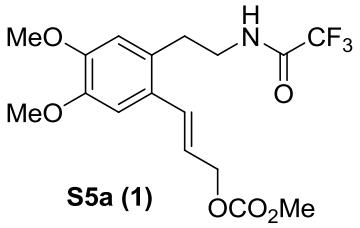
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N
CF3
O
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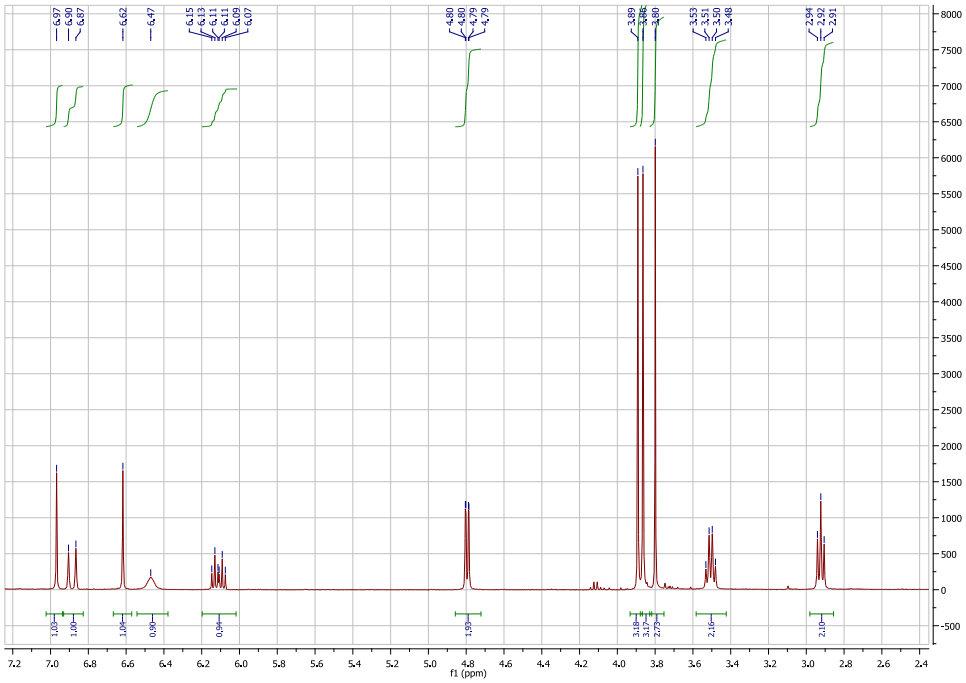
**S5a (1)**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4.79
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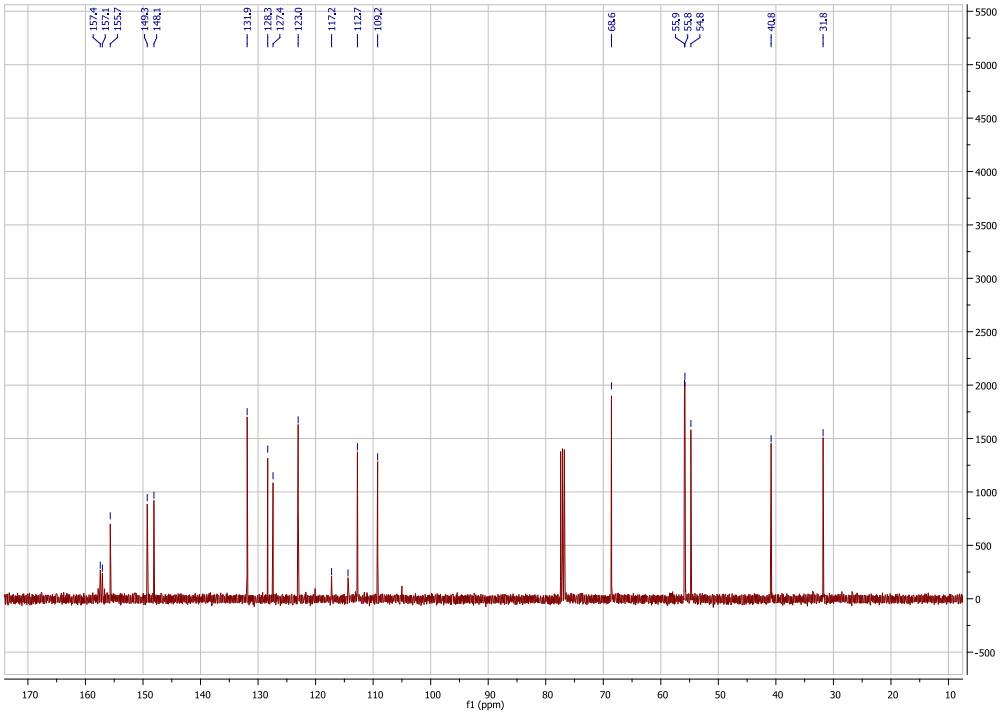
f1 (ppm)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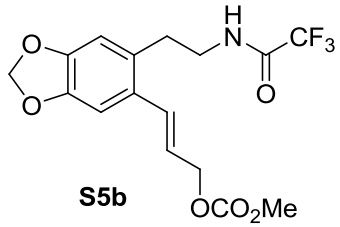
f1 (ppm)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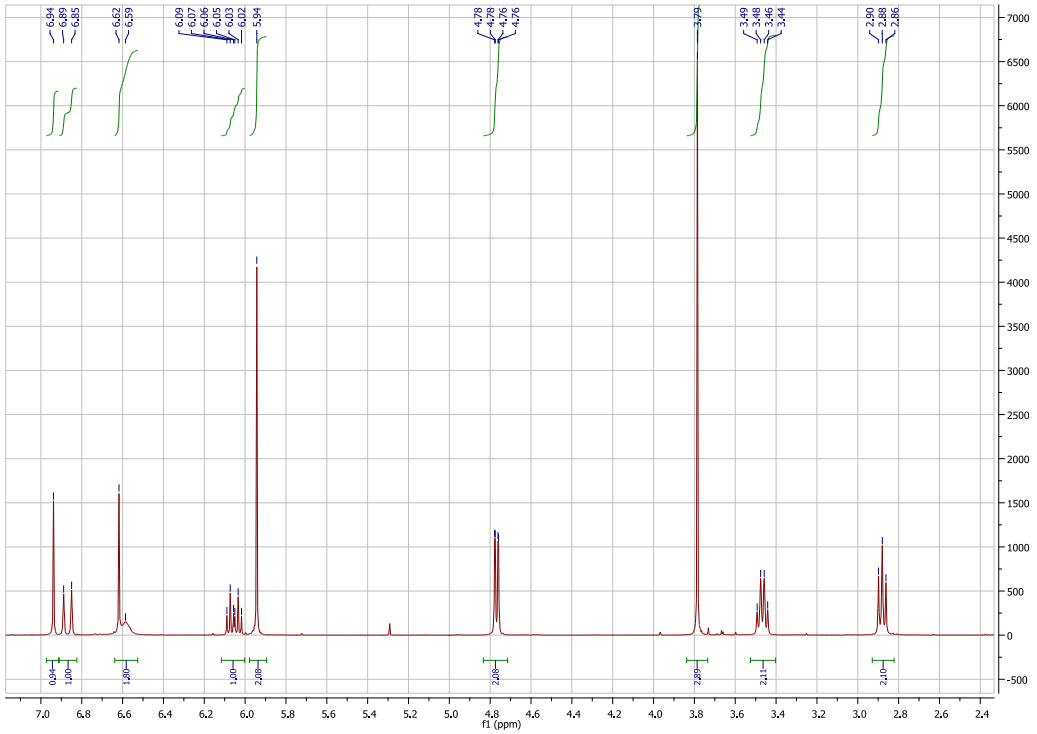
**S5b**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3.79
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3.46
3.44
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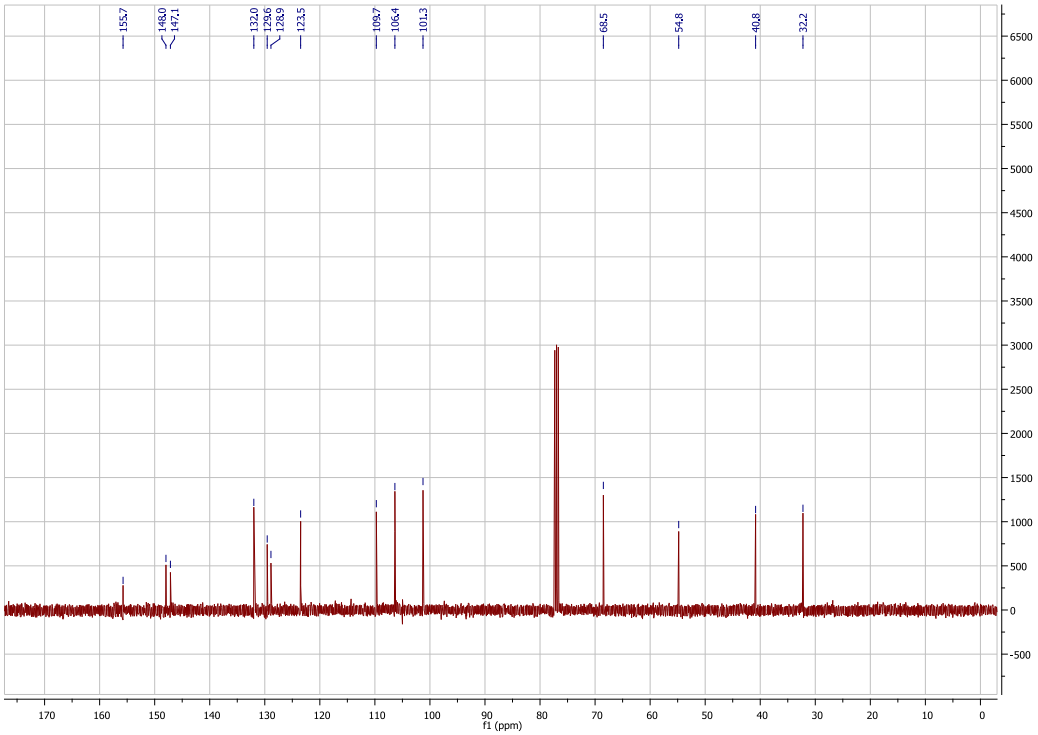
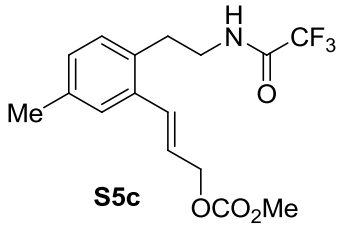
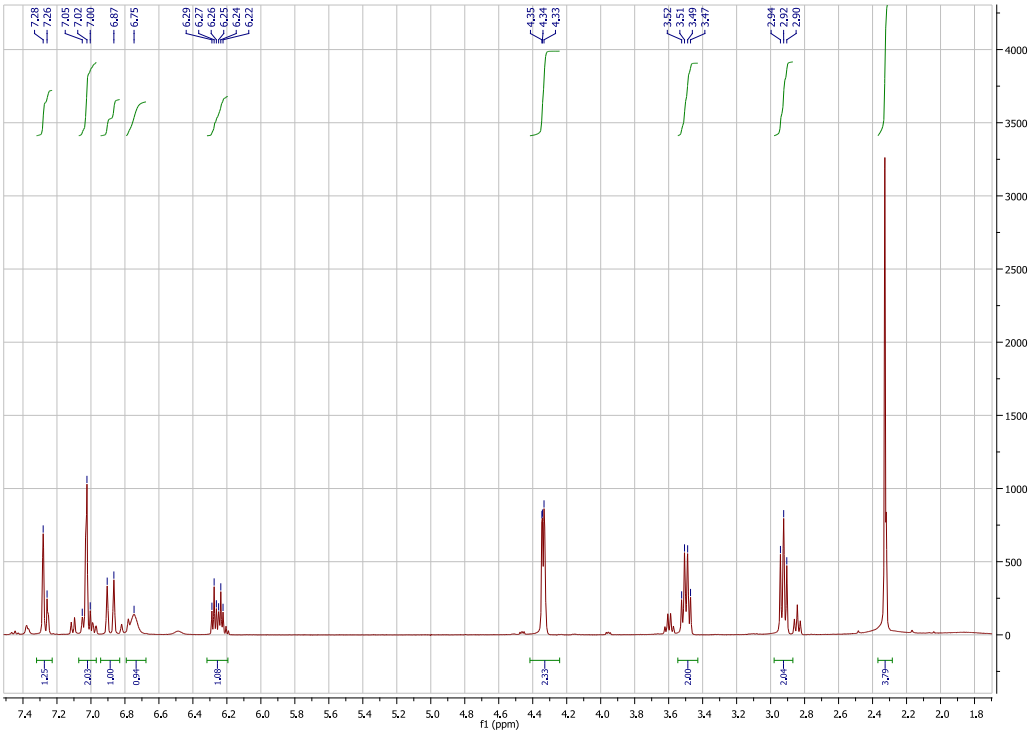
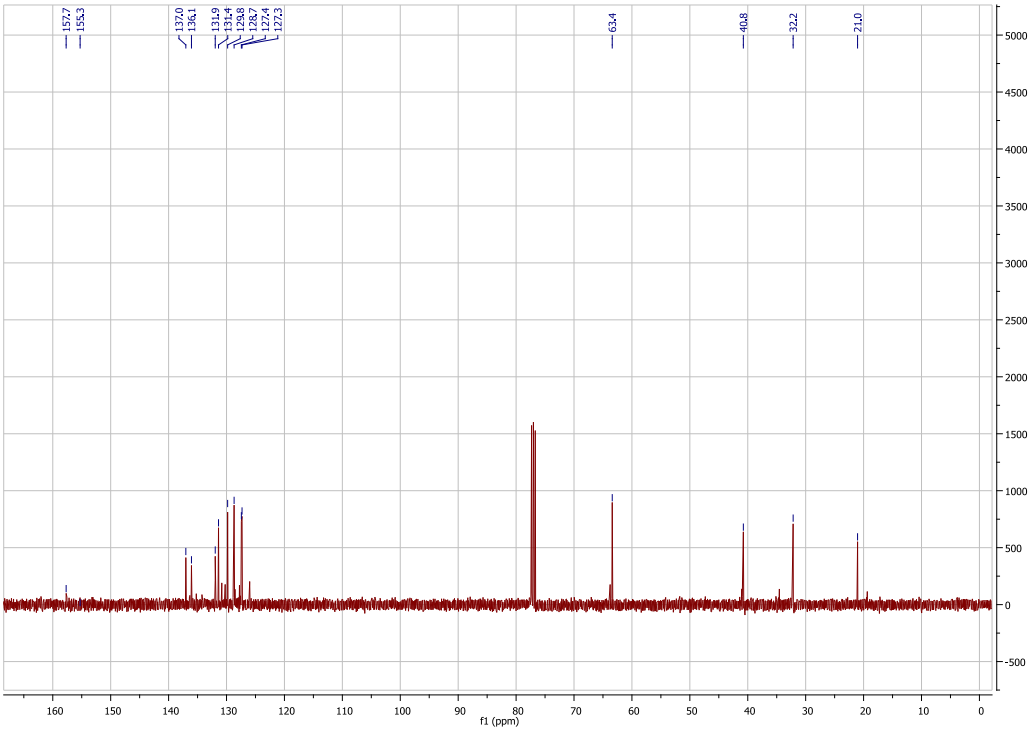
2.88
2.86
0.94
1.00
1.80
1.00
2.08
2.08
2.89
2.11
2.10
f1 (ppm)

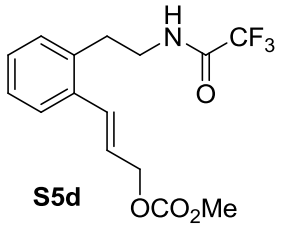

155.7
148.0
147.1
132.0
125.6
128.9
123.5
109.7
106.4
101.3
68.5
54.8
40.8
32.2
f1 (ppm)


H
N
CF3
O
Me
OCO2Me

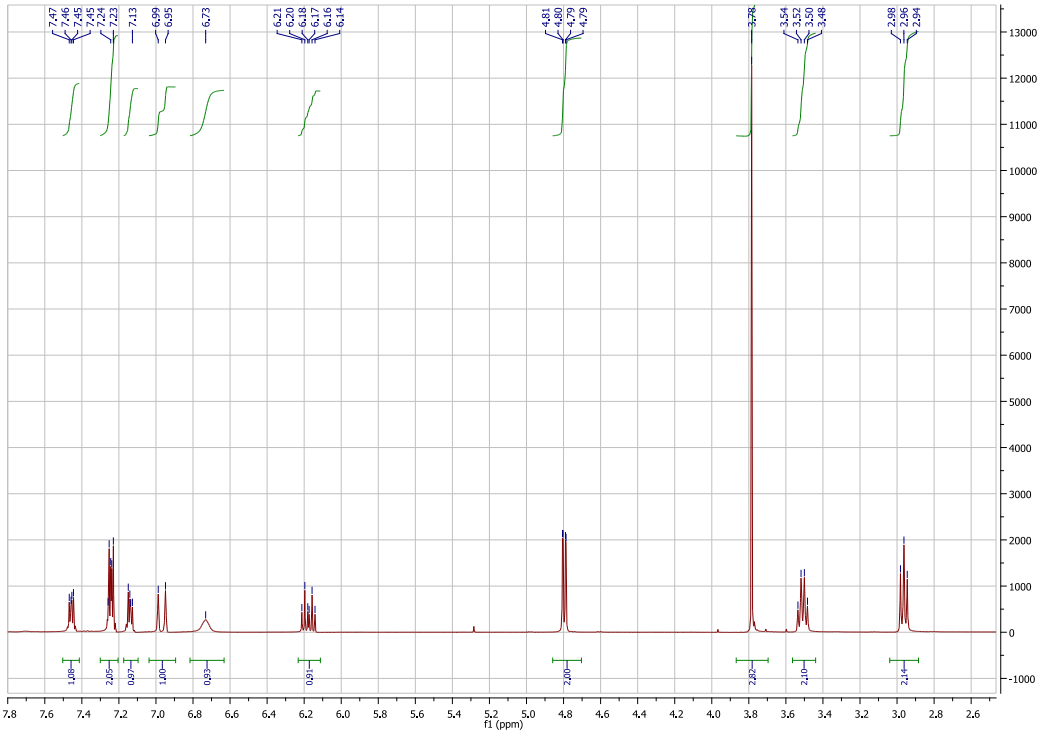
**S5c**

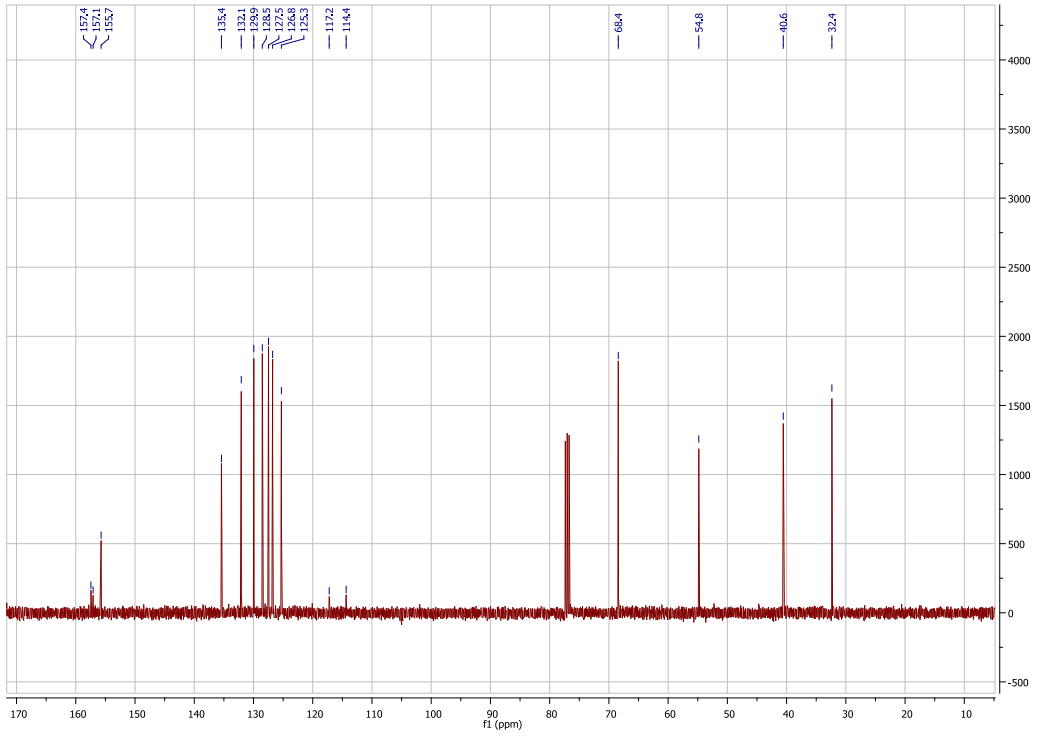

7.28
7.26
7.05
7.02
7.00
6.87
6.75
6.29
6.27
6.26
6.25
6.24
6.22
4.35
4.34
4.33
3.52
3.51
3.49
3.47
2.94
2.92
2.90
1.25
2.03
1.00
0.94
1.08
2.33
2.00
2.04
3.79
f1 (ppm)

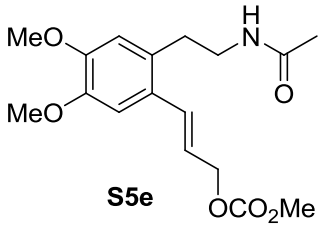

157.7
155.3
137.0
136.1
131.9
129.4
128.8
128.7
127.4
127.3
63.4
40.8
32.2
21.0
f1 (ppm)


H
N
CF3
O
OCO2Me

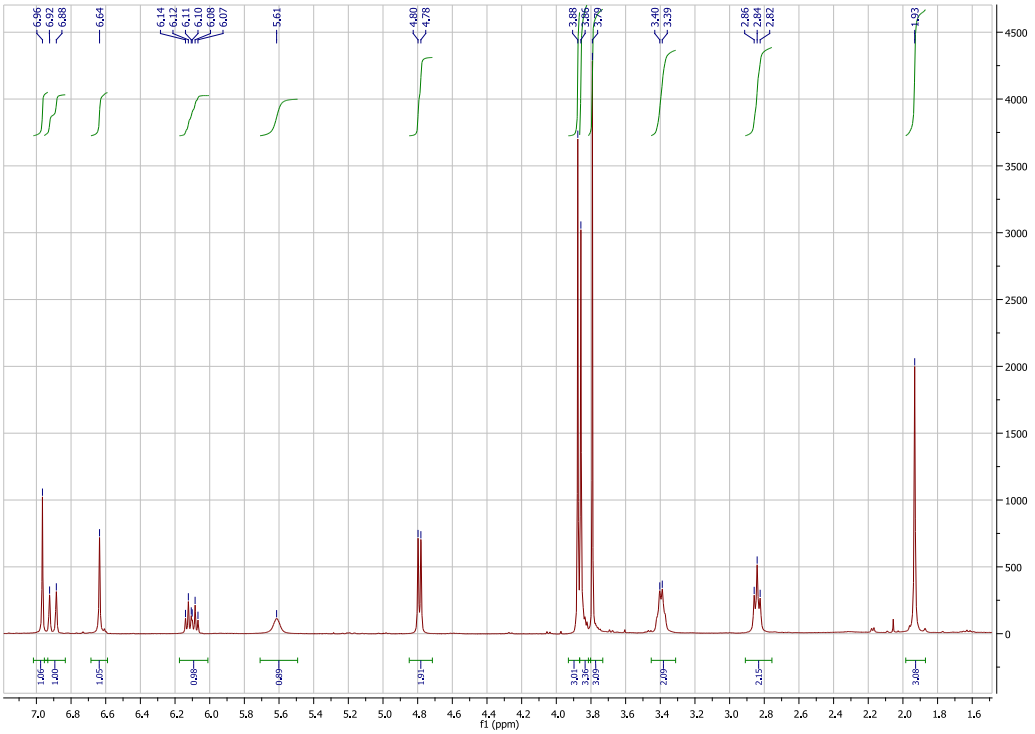
**S5d**

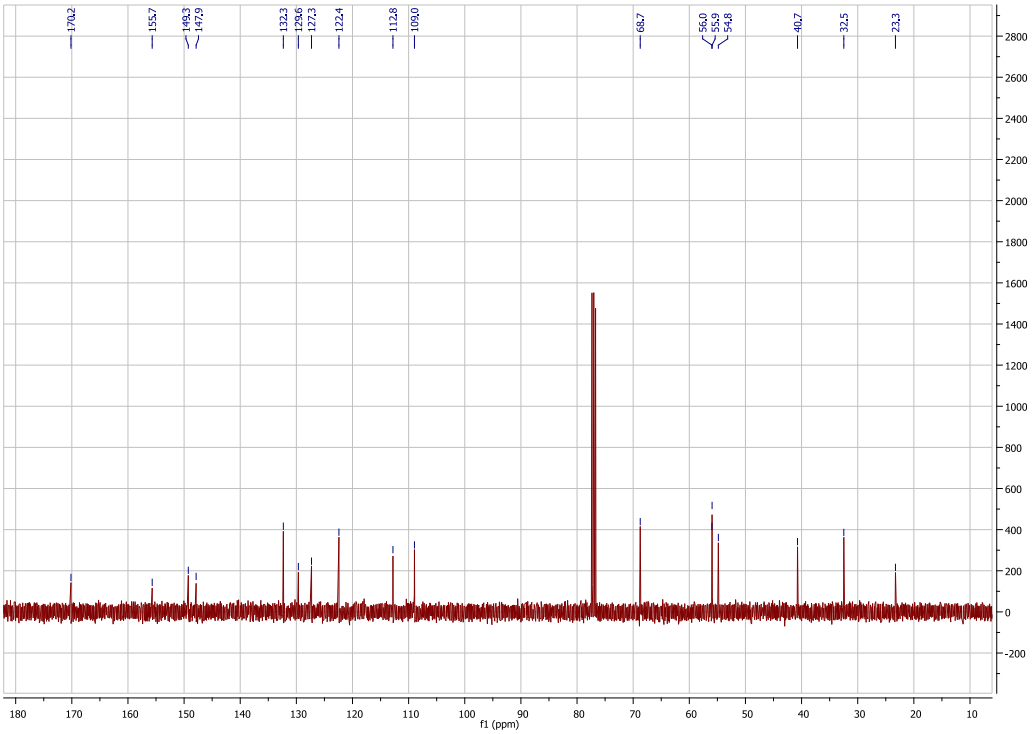

7.47
7.46
7.45
7.45
7.24
7.23
7.13
6.99
6.95
6.73
6.21
6.20
6.18
6.17
6.16
6.14
4.81
4.80
4.79
4.79
3.78
3.54
3.52
3.50
3.48
2.98
2.96
2.94
1.08
2.05
0.97
1.00
0.93
0.91
2.00
2.82
2.10
2.14
f1 (ppm)

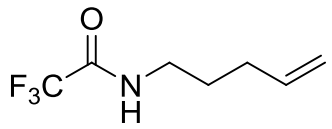

157.4
157.1
155.7
135.4
132.1
129.9
128.5
127.5
126.8
125.3
117.2
114.4
68.4
54.8
40.6
32.4
f1 (ppm)


MeO
MeO
H
N
O
OCO2Me

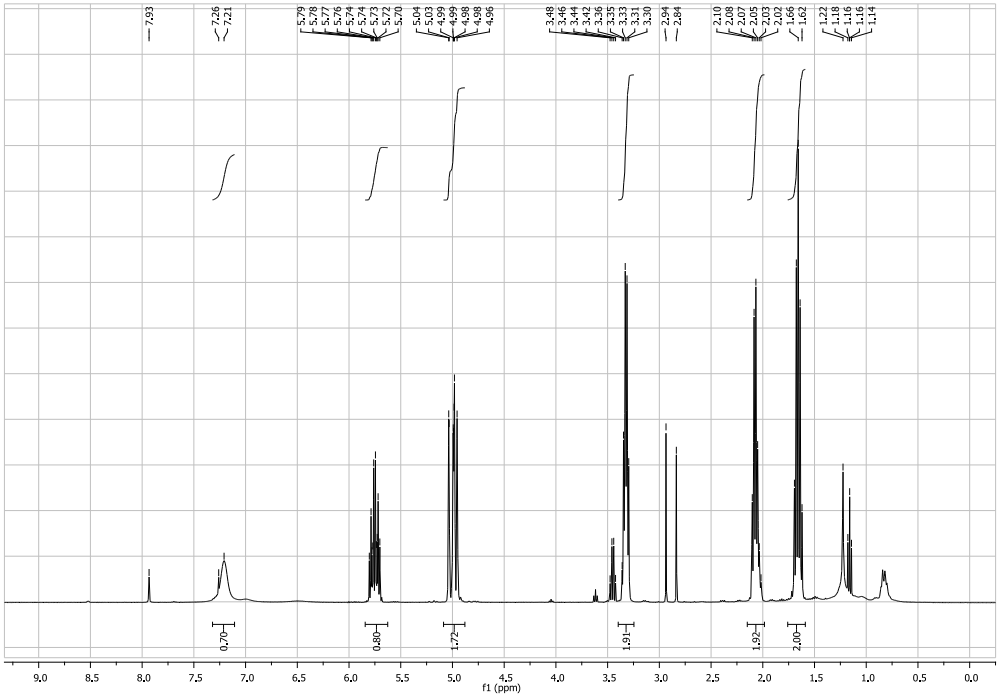
**S5e**

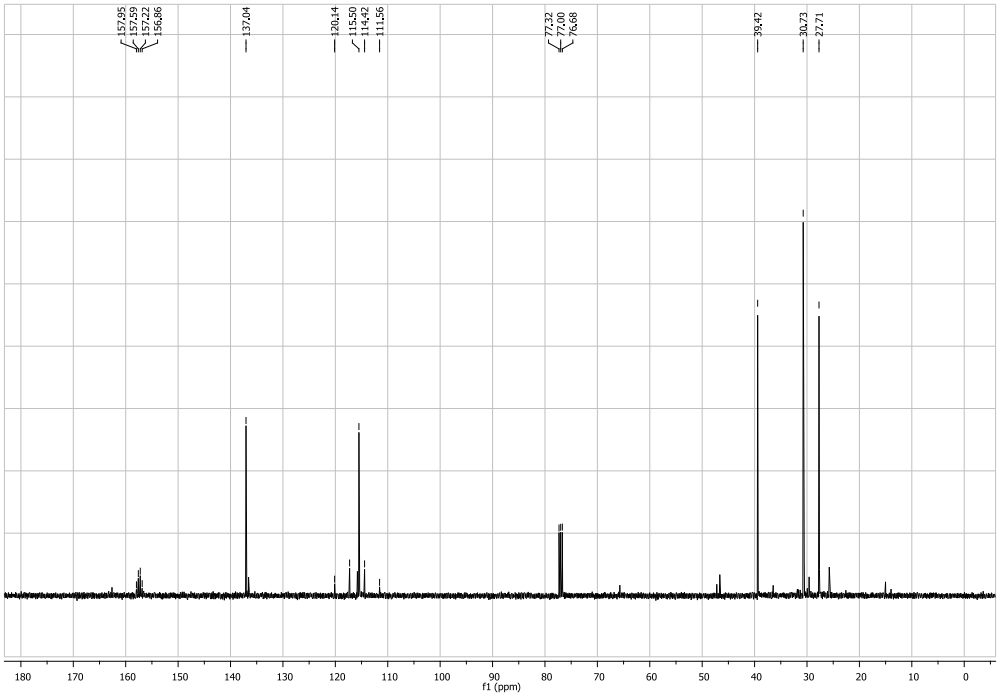

6.96
6.92
6.88
6.64
6.14
6.12
6.11
6.10
6.08
6.07
5.61
4.80
4.78
3.88
3.86
3.79
3.40
3.39
2.86
2.84
2.82
1.93
f1 (ppm)

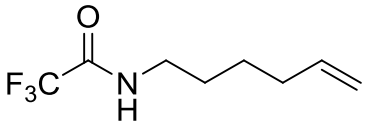

170.2
155.7
149.3
147.9
132.3
129.6
127.3
122.4
112.8
109.0
68.7
56.0
55.9
54.8
40.7
32.5
23.3
f1 (ppm)



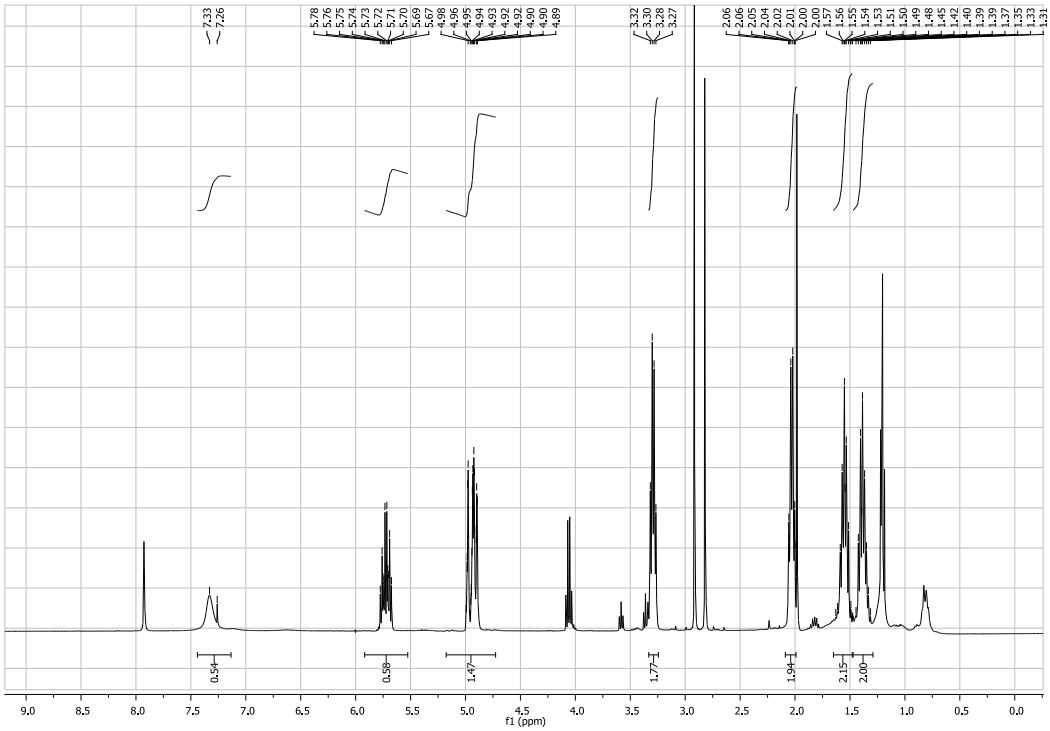
**S6a**

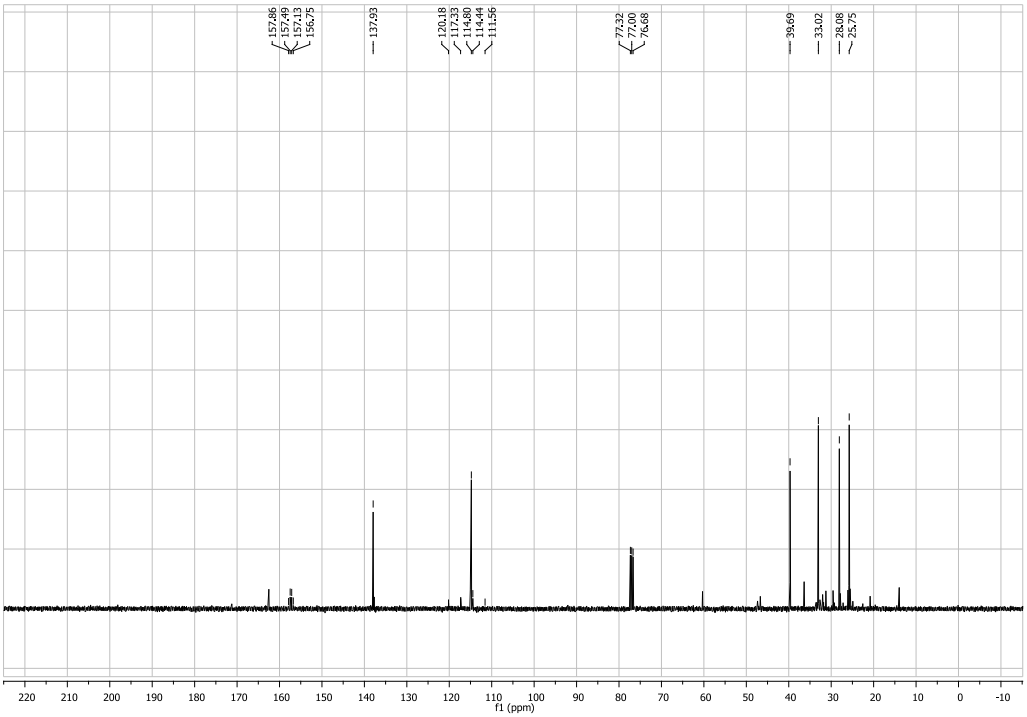


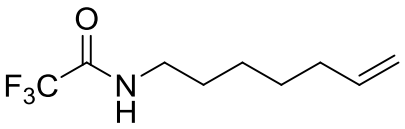




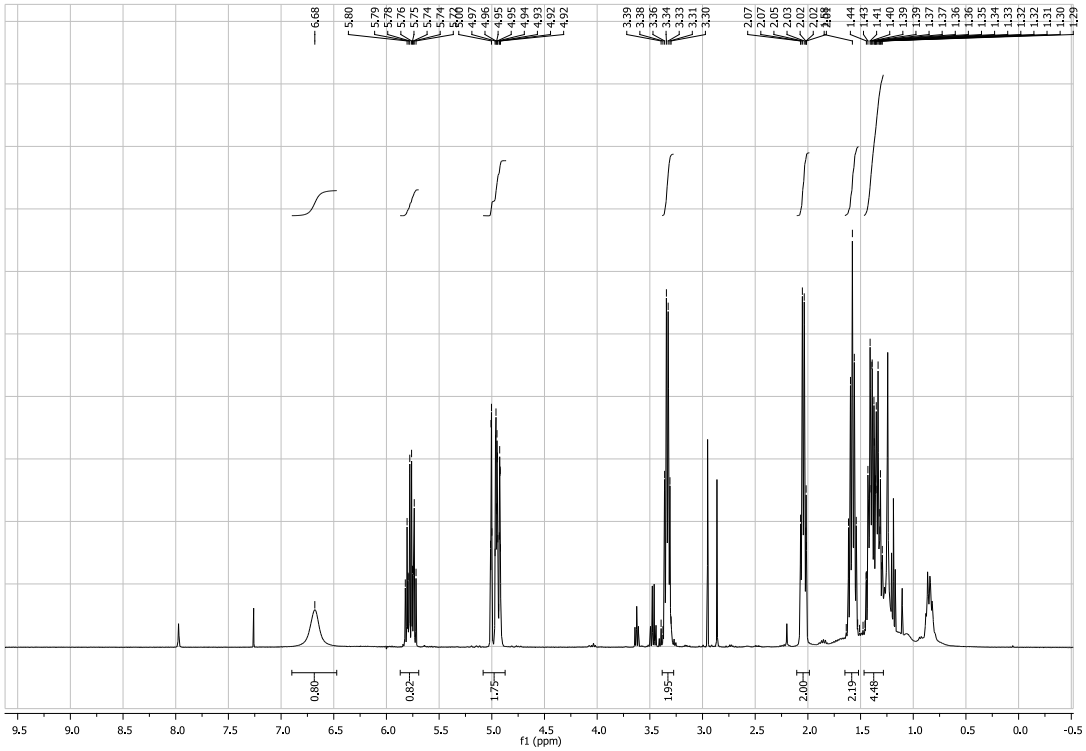
**S6b**

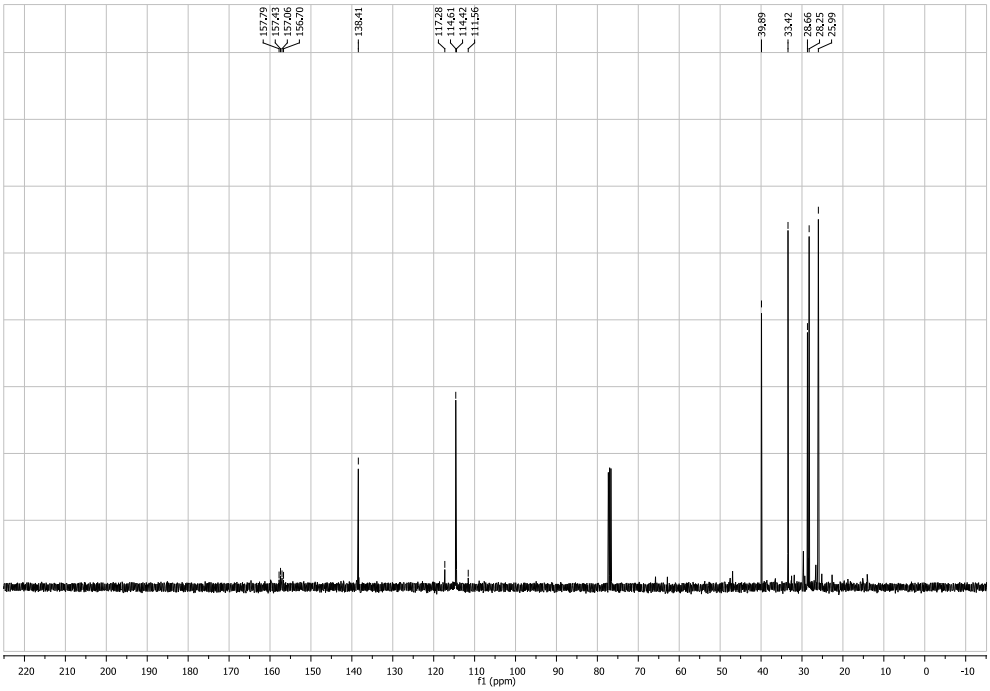


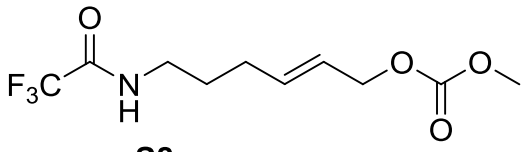




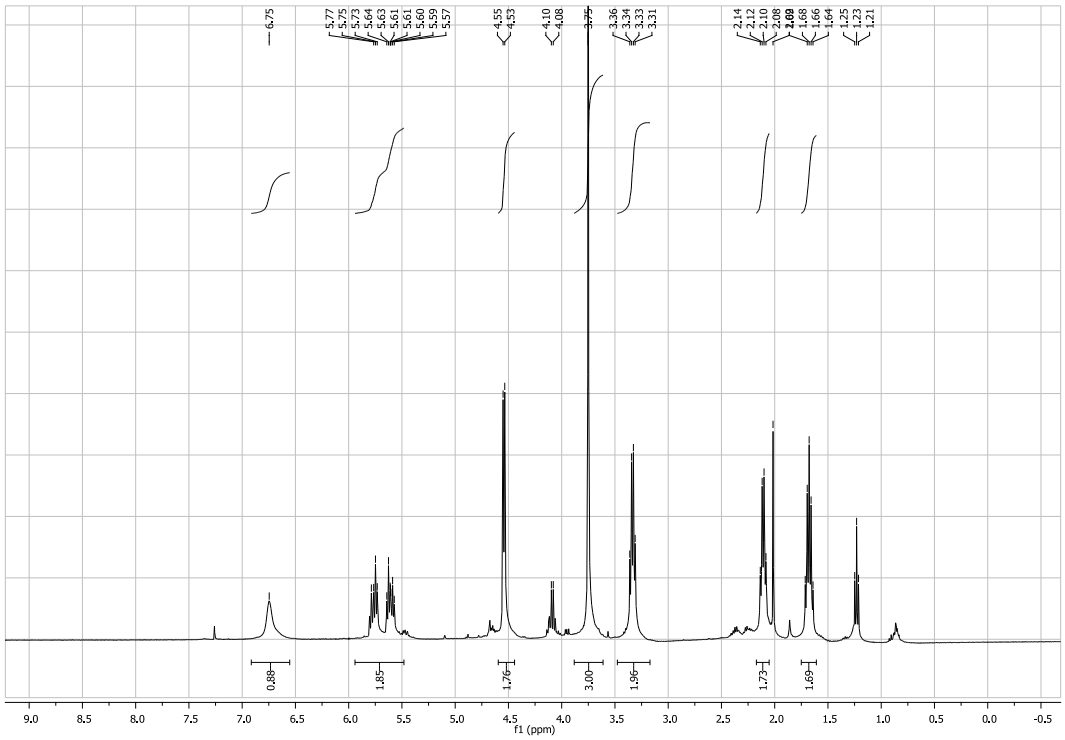
**S6c**

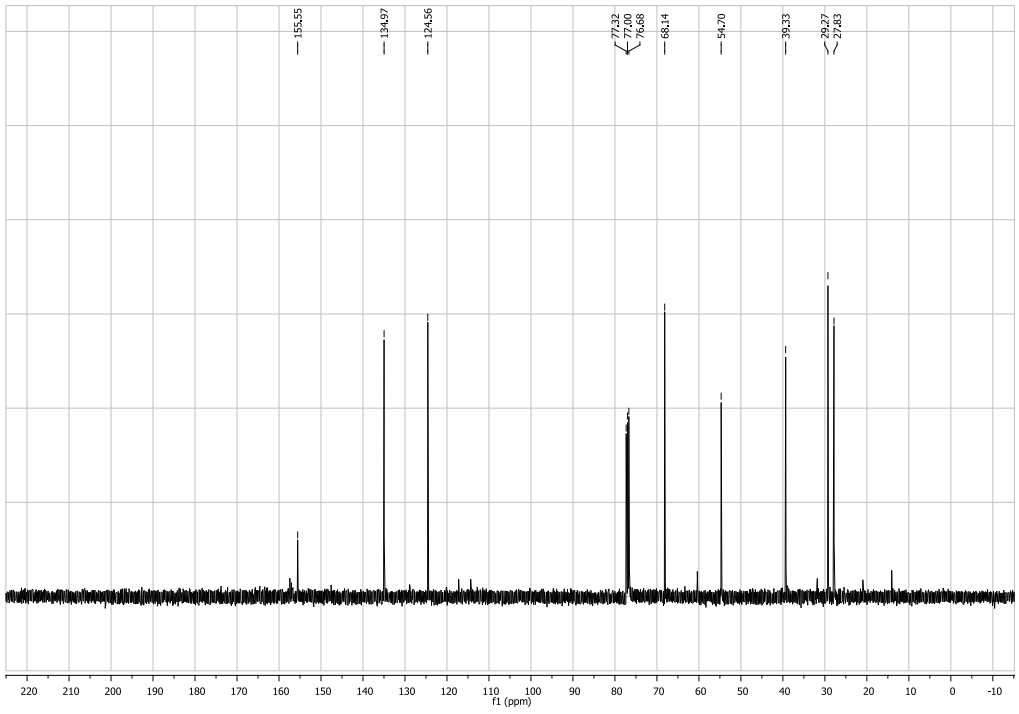

6.68
5.80
5.79
5.78
5.76
5.75
5.74
5.74
5.00
4.97
4.96
4.95
4.95
4.94
4.93
4.92
4.92
3.39
3.38
3.36
3.34
3.33
3.31
3.30
2.07
2.07
2.05
2.03
2.02
2.02
1.44
1.43
1.41
1.40
1.39
1.39
1.37
1.37
1.36
1.36
1.35
1.34
1.33
1.32
1.32
1.31
1.30
1.29
0.80
0.82
1.75
1.95
2.00
2.19
4.48
f1 (ppm)

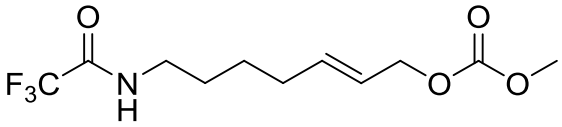

157.79
157.43
157.06
156.70
138.41
117.28
114.61
114.27
111.56
39.89
33.42
28.66
28.25
25.99
f1 (ppm)



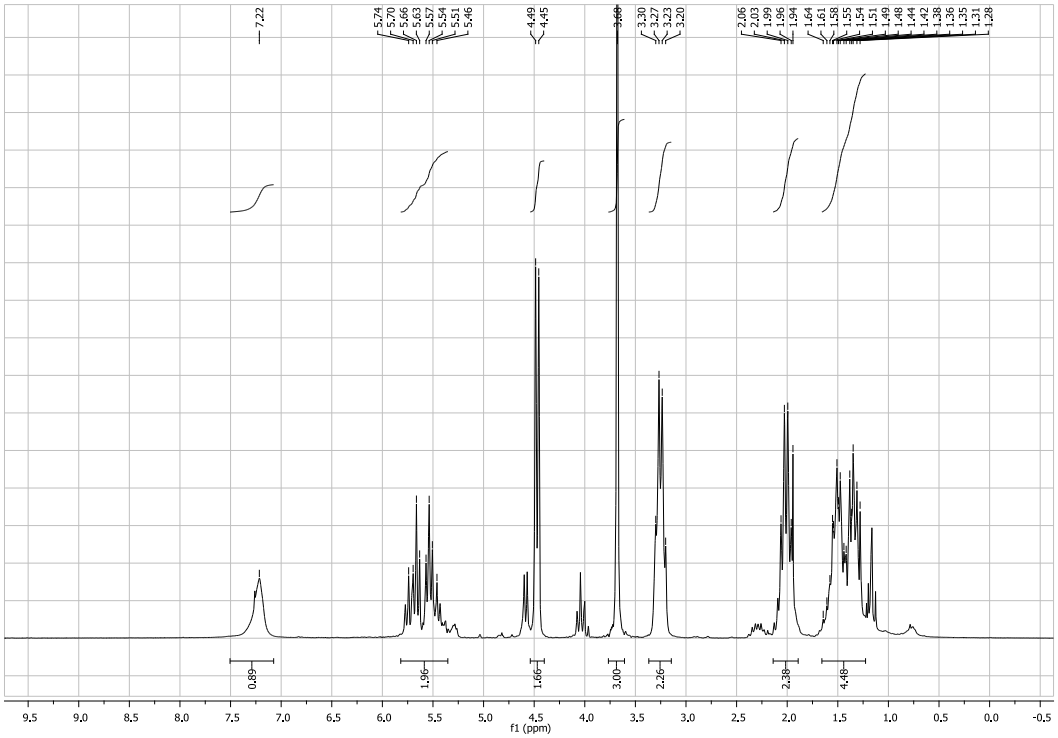
**S8a**

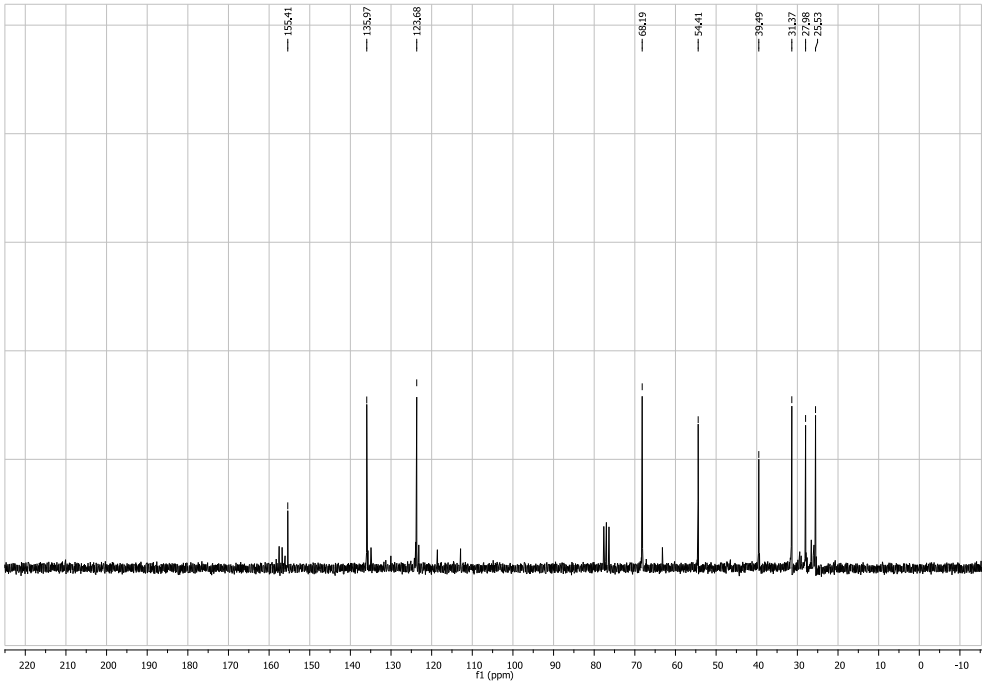

6.75
5.77
5.75
5.73
5.64
5.63
5.61
5.61
5.60
5.59
5.57
4.55
4.53
4.10
4.08
3.75
3.36
3.34
3.33
3.31
2.14
2.12
2.10
2.08
1.68
1.66
1.64
1.25
1.23
1.21
0.88
1.85
1.76
3.00
1.96
1.73
1.69
f1 (ppm)

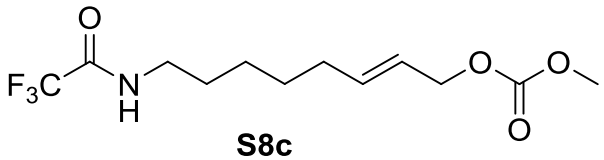

155.55
134.97
124.56
77.32
77.00
76.68
68.14
54.70
39.33
29.27
27.83
f1 (ppm)



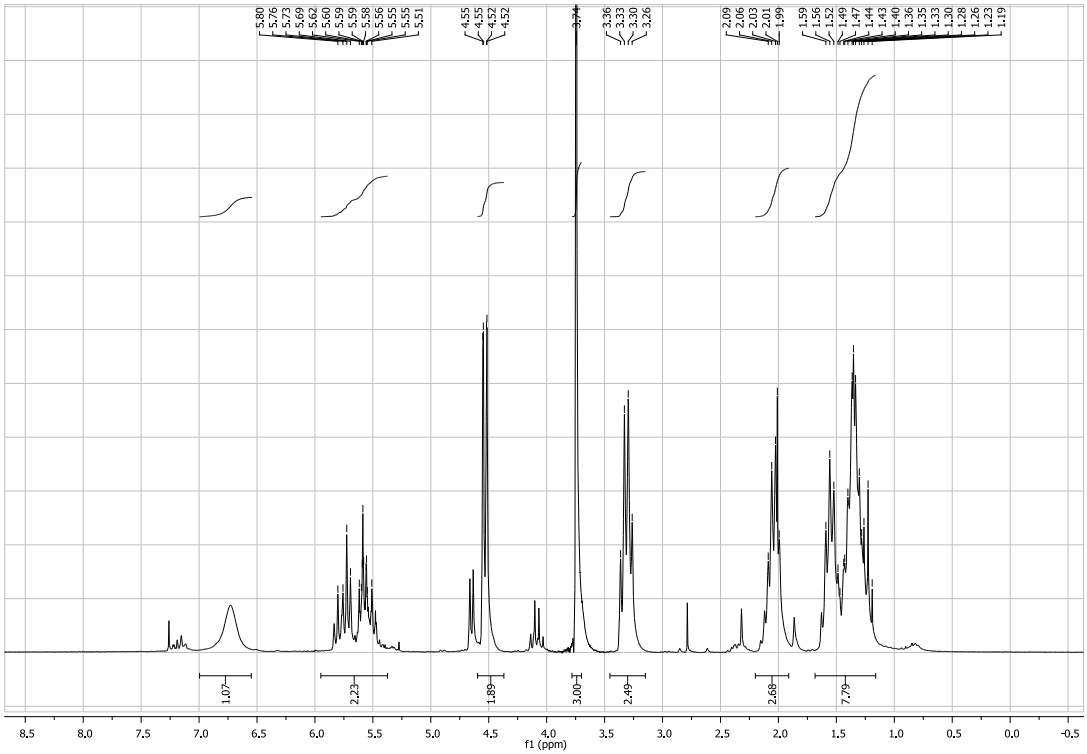
**S8b**

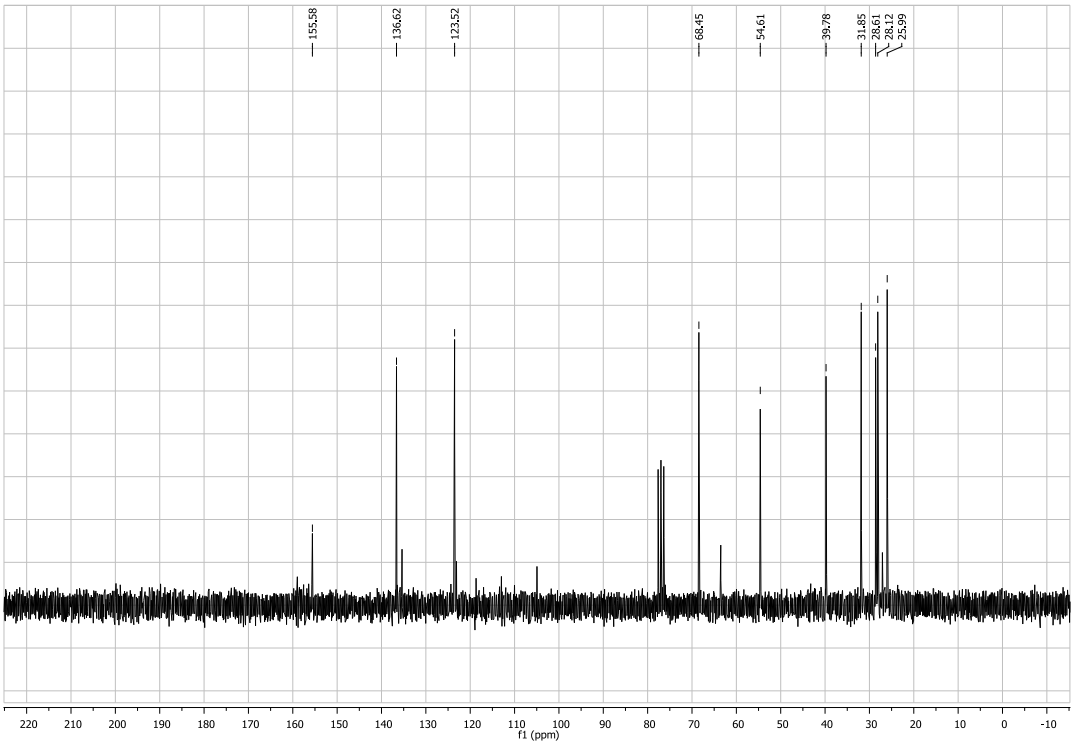

7.22
5.74
5.70
5.66
5.63
5.57
5.54
5.51
5.46
4.49
4.45
3.68
3.30
3.27
3.23
3.20
2.06
2.03
1.99
1.96
1.94
1.64
1.61
1.58
1.55
1.54
1.51
1.49
1.48
1.44
1.42
1.38
1.36
1.35
1.31
1.28
0.89
1.96
1.66
3.00
2.26
2.38
4.48
f1 (ppm)

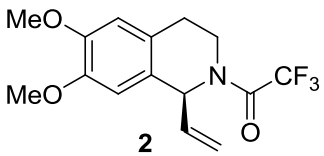

155.41
135.97
123.68
68.19
54.41
39.49
31.37
27.98
25.53
f1 (ppm)



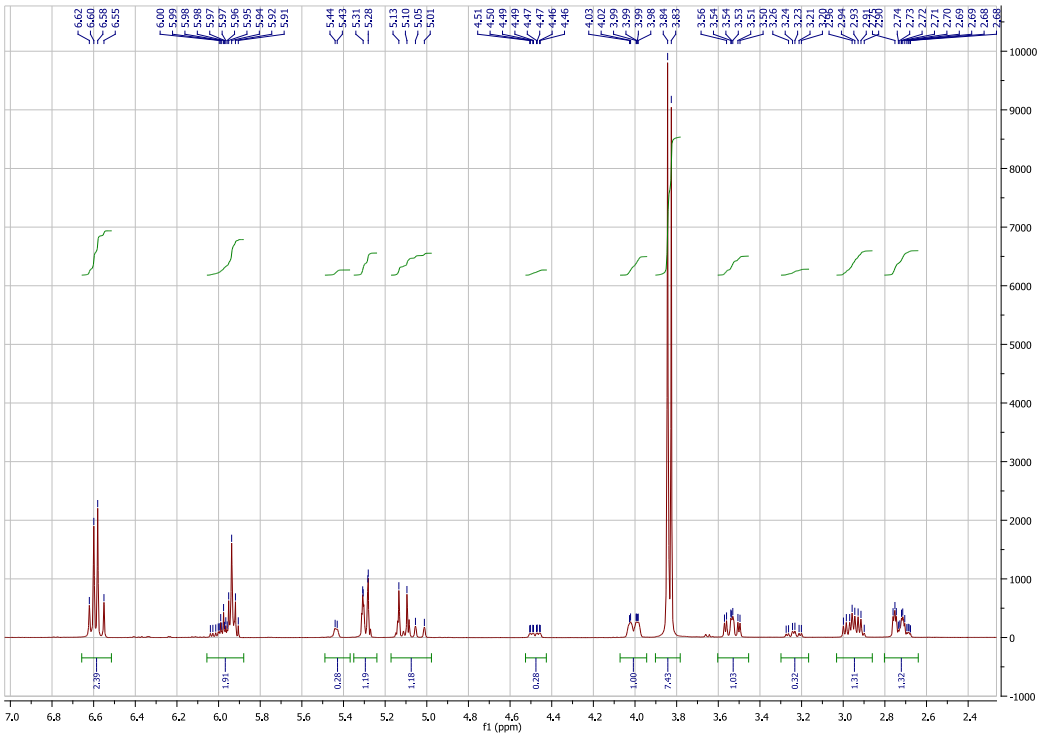
**S8c**

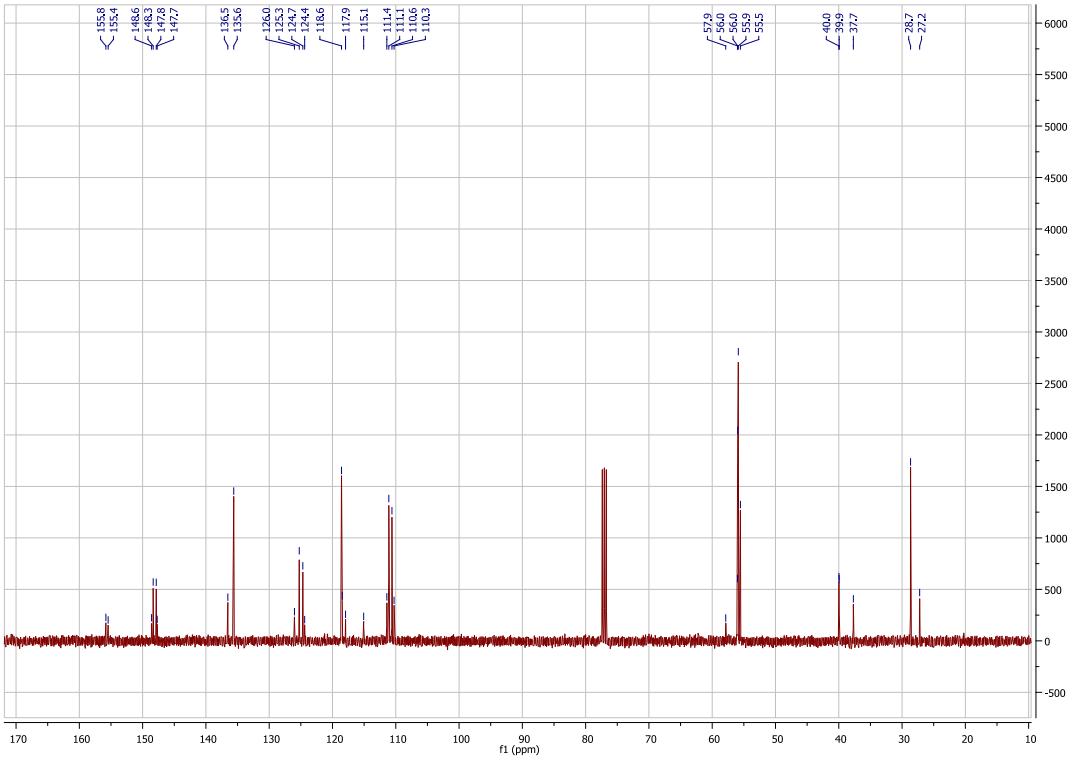


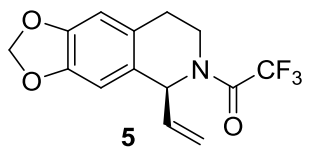





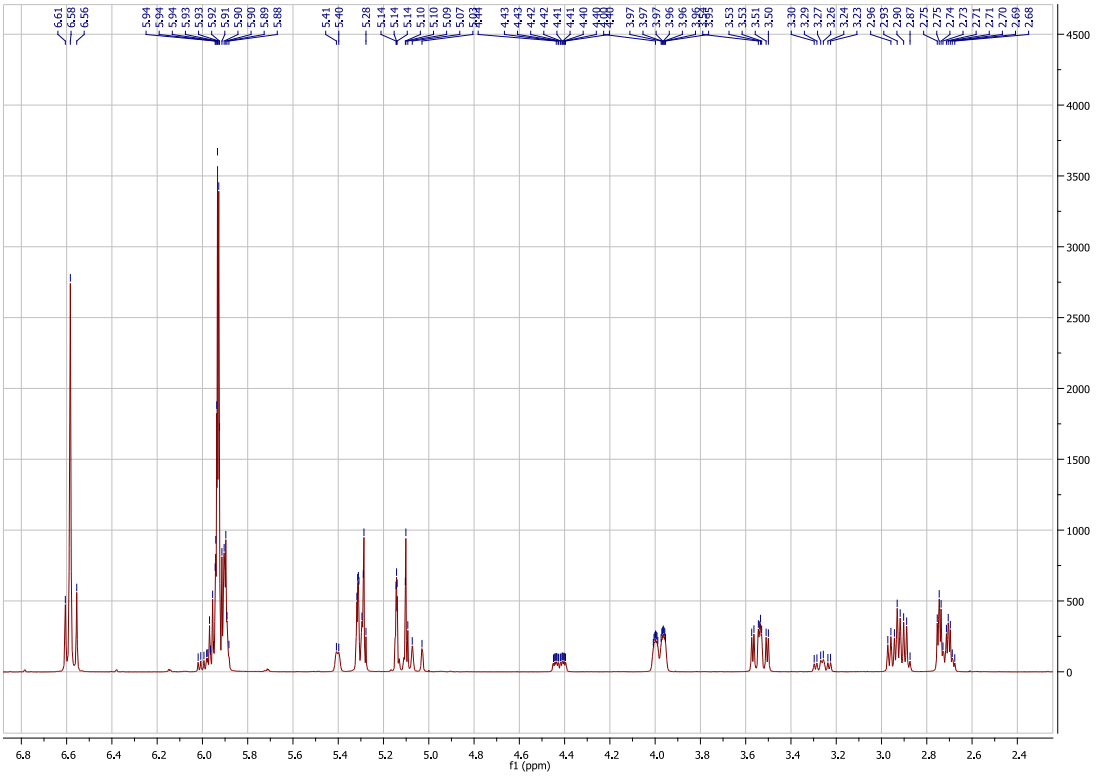

**2**

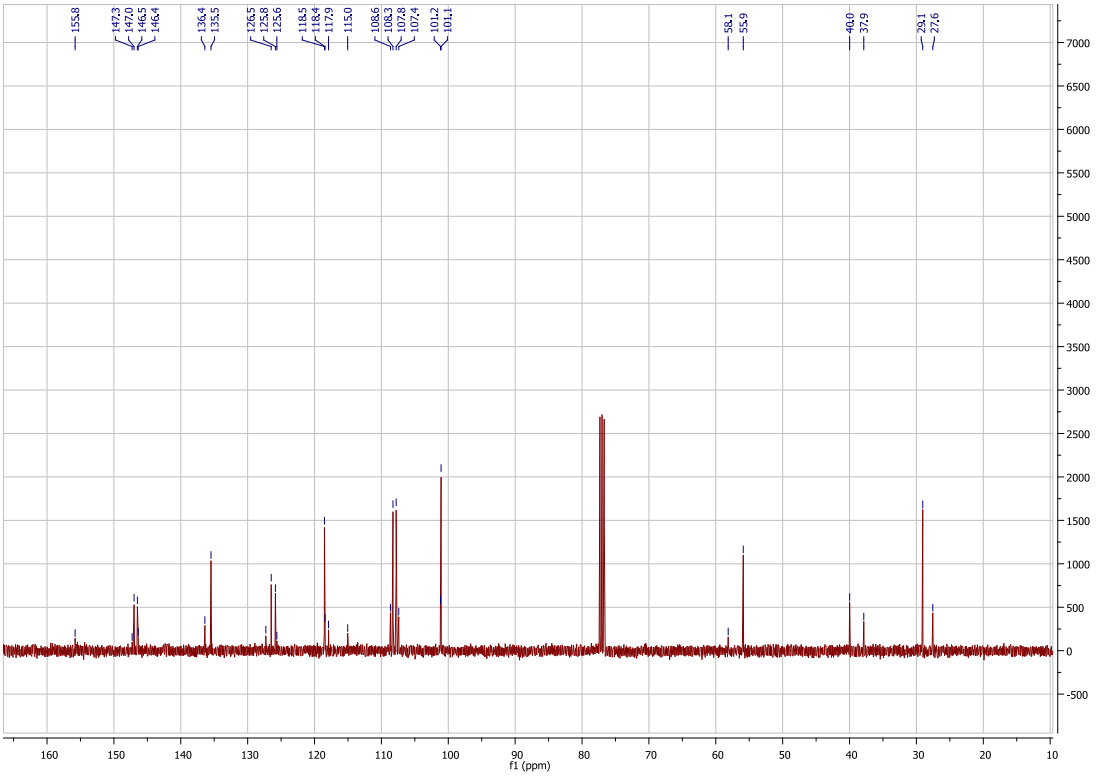


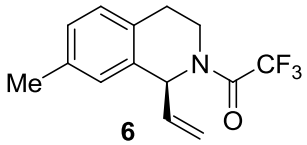





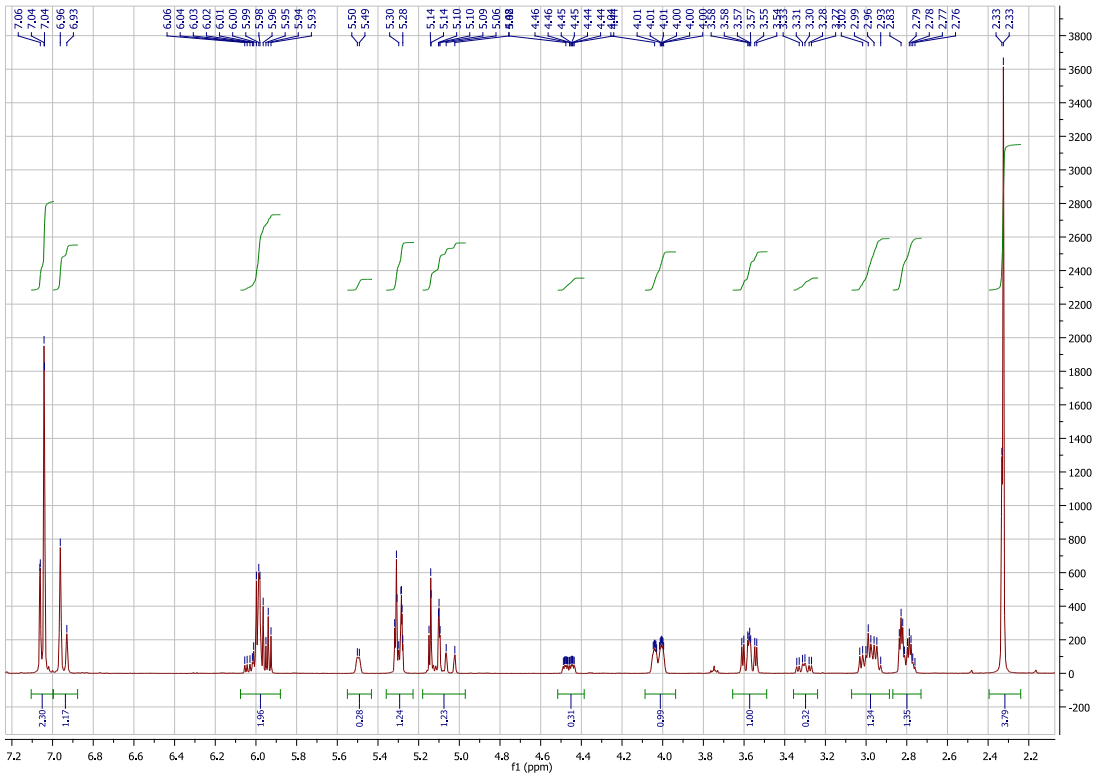

**5**

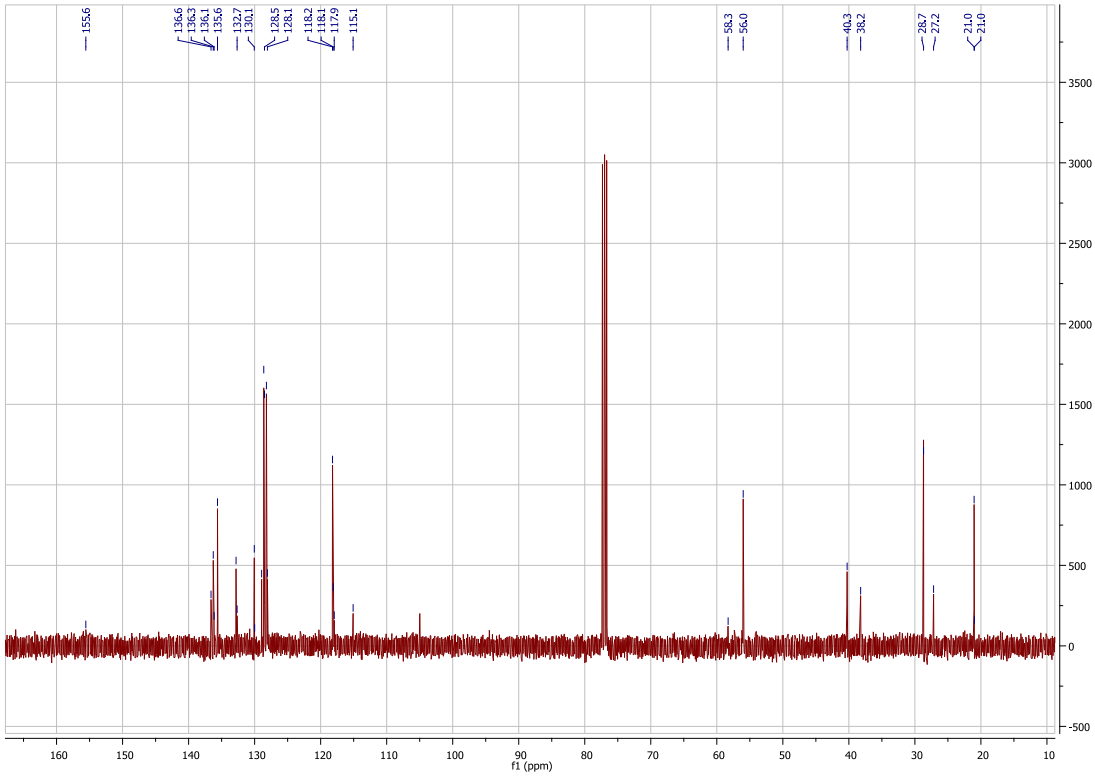


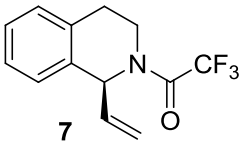





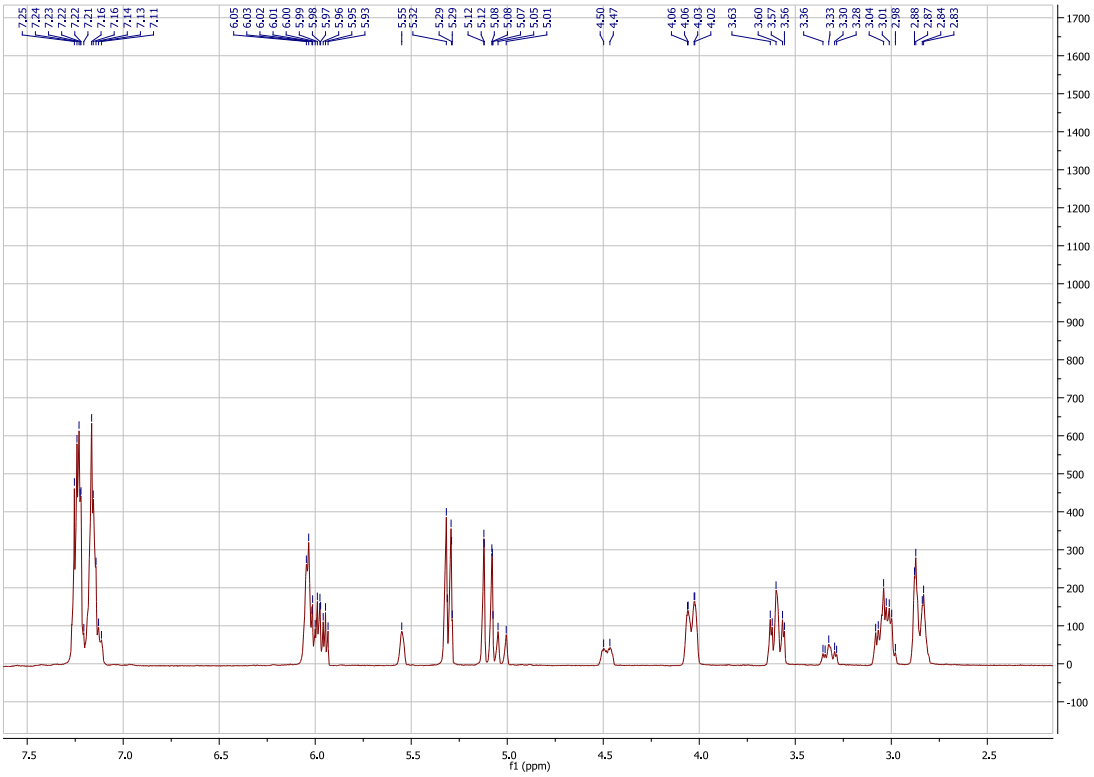

**6**

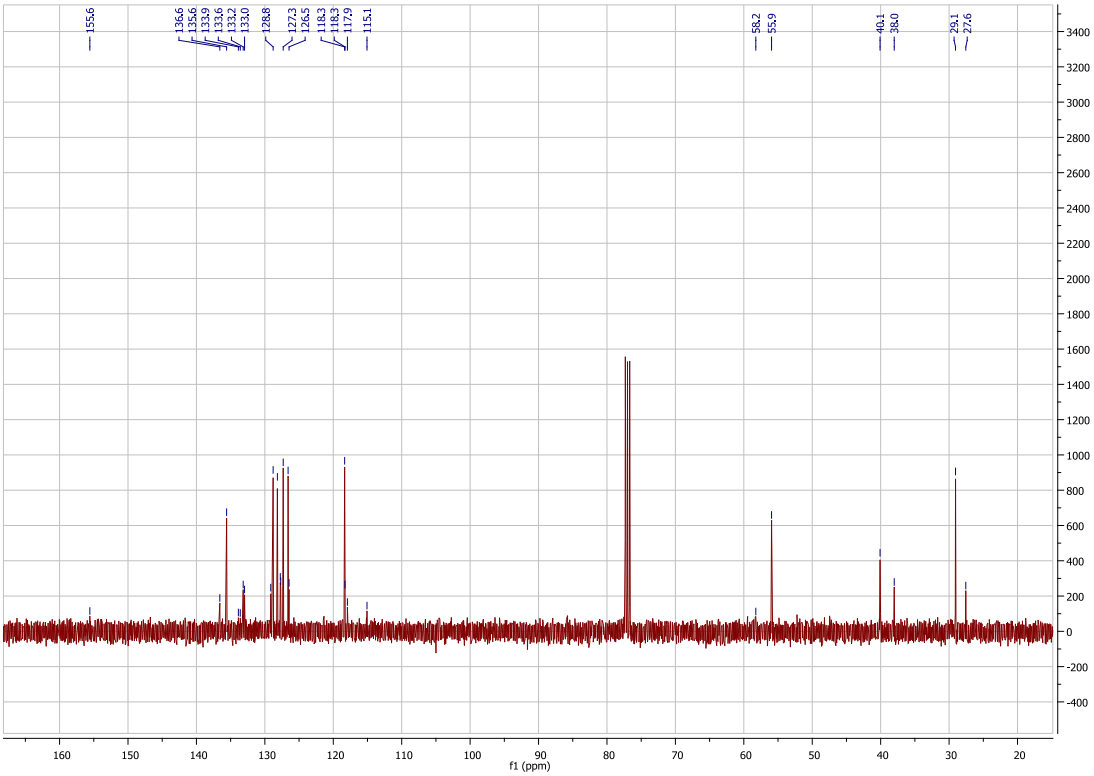


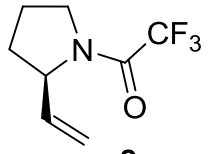




N
CF3
O

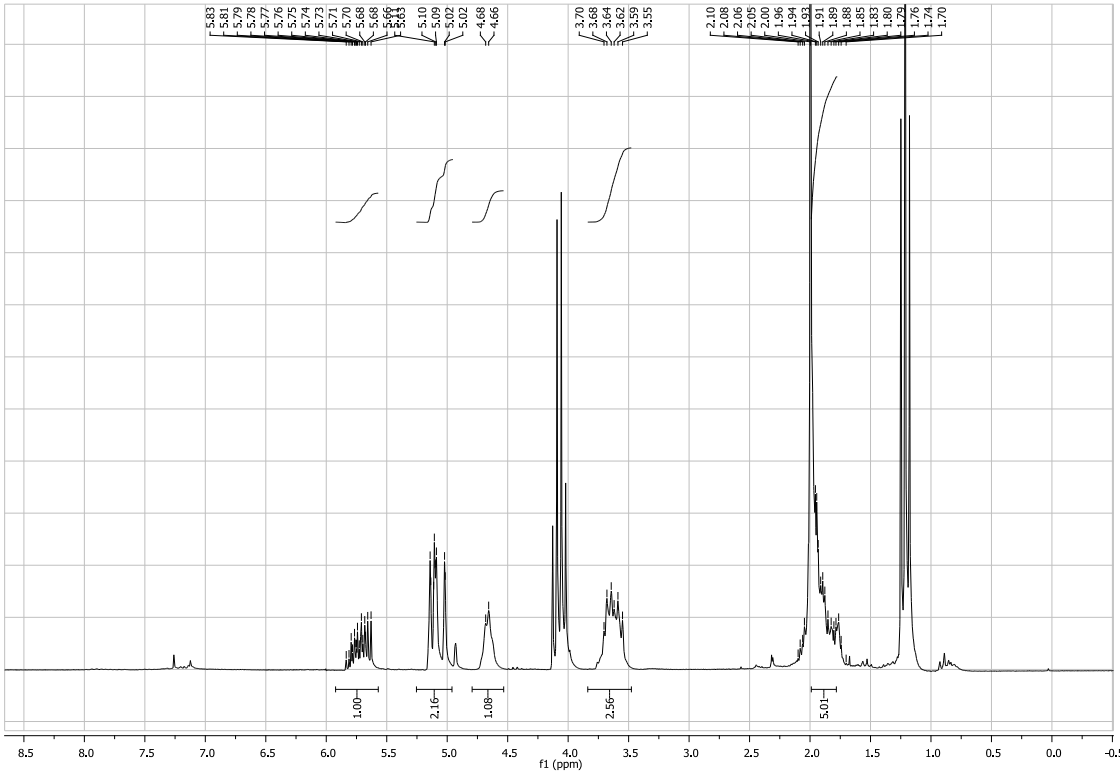
**7**


7.25 7.24 7.23 7.22 7.22 7.21 7.16 7.16 7.14 7.13 7.11
6.05 6.03 6.02 6.01 6.00 5.99 5.98 5.97 5.96 5.95 5.93
5.55 5.52 5.29 5.29 5.12 5.12 5.08 5.08 5.07 5.05 5.01
4.50 4.47
4.06 4.06 4.03 4.02
3.63
3.60 3.57 3.56
3.36
3.33 3.30 3.28 3.04 3.01 2.98
2.88 2.87 2.84 2.83
f1 (ppm)


155.6
136.6 135.6 133.9 133.6 133.2 133.0 128.8 127.3 126.5 118.3 118.3 117.9 115.1
58.2 55.9
40.1 38.0
29.1 27.6
f1 (ppm)


N
CF3
O

**8**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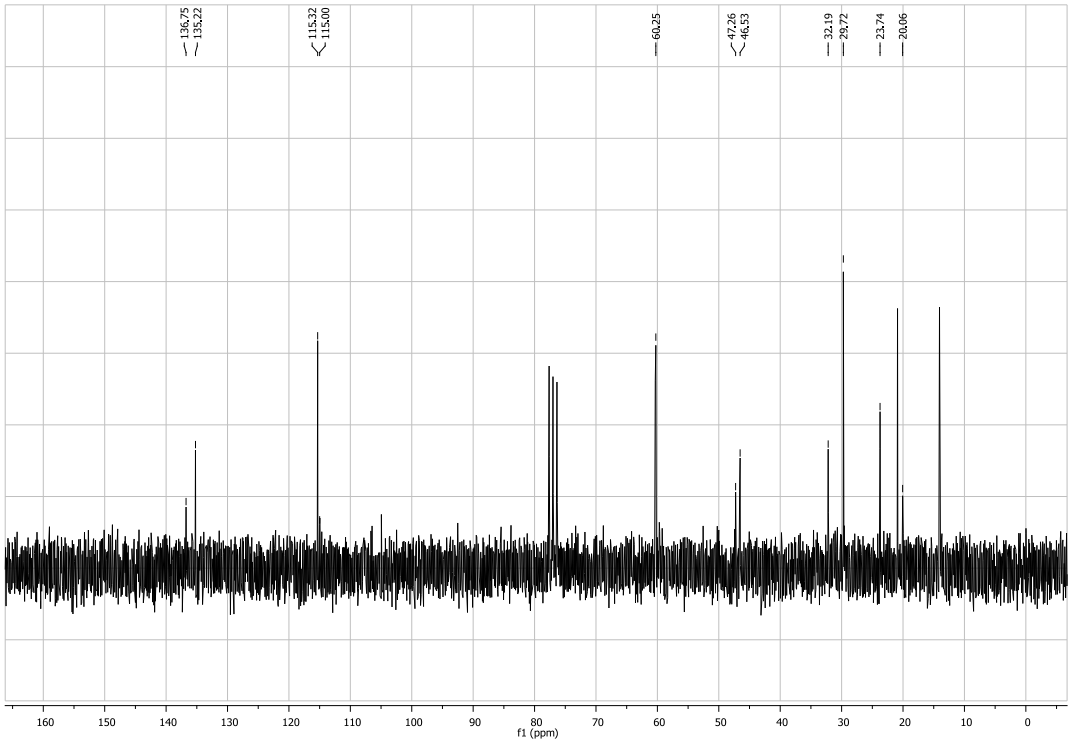
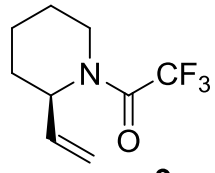
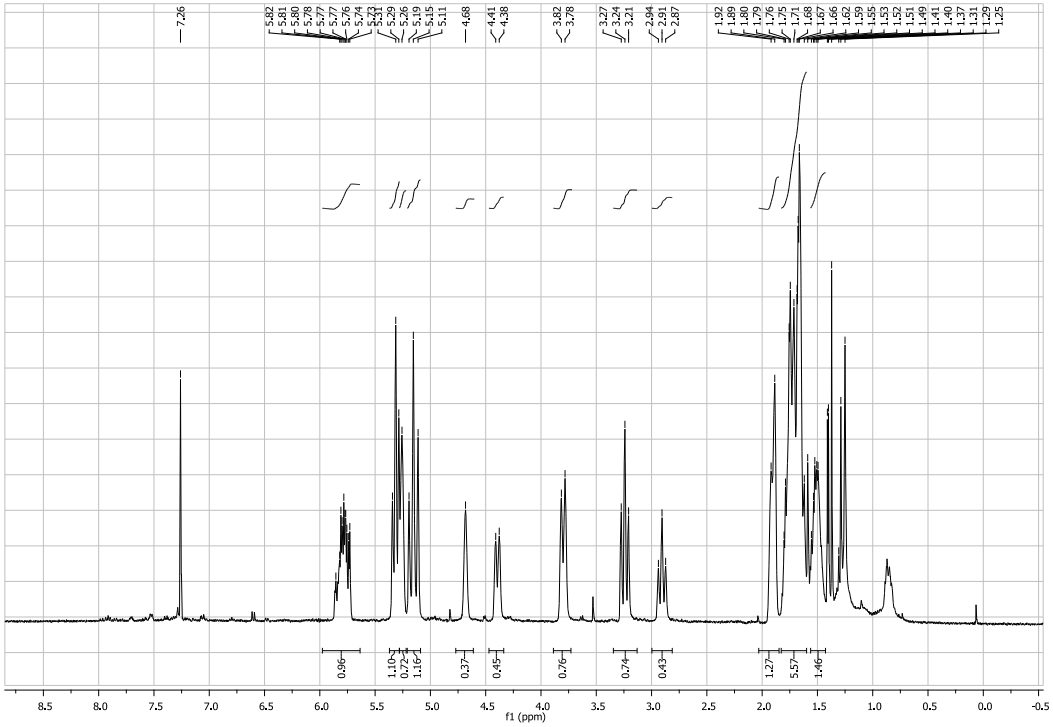
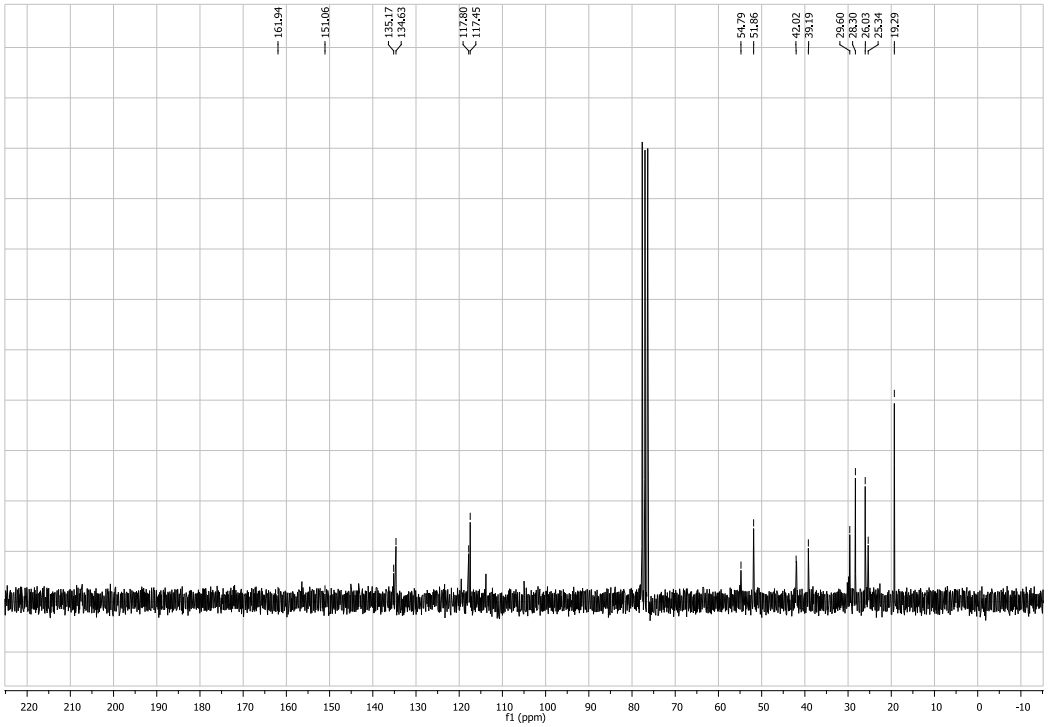
5.78
5.77
5.76
5.75
5.74
5.73
5.71
5.70
5.68
5.68
5.66
5.65
5.63
5.10
5.09
5.02
5.02
4.68
4.66
3.70
3.68
3.64
3.62
3.59
3.55
2.10
2.08
2.06
2.05
2.00
1.96
1.94
1.93
1.91
1.89
1.88
1.85
1.83
1.80
1.79
1.76
1.74
1.70
1.00
2.16
1.08
2.56
5.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

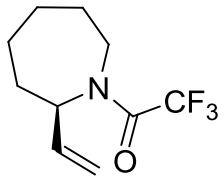

136.75
135.22
115.32
115.00
60.25
47.26
46.53
32.19
29.72
23.74
20.06
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
CF3
O

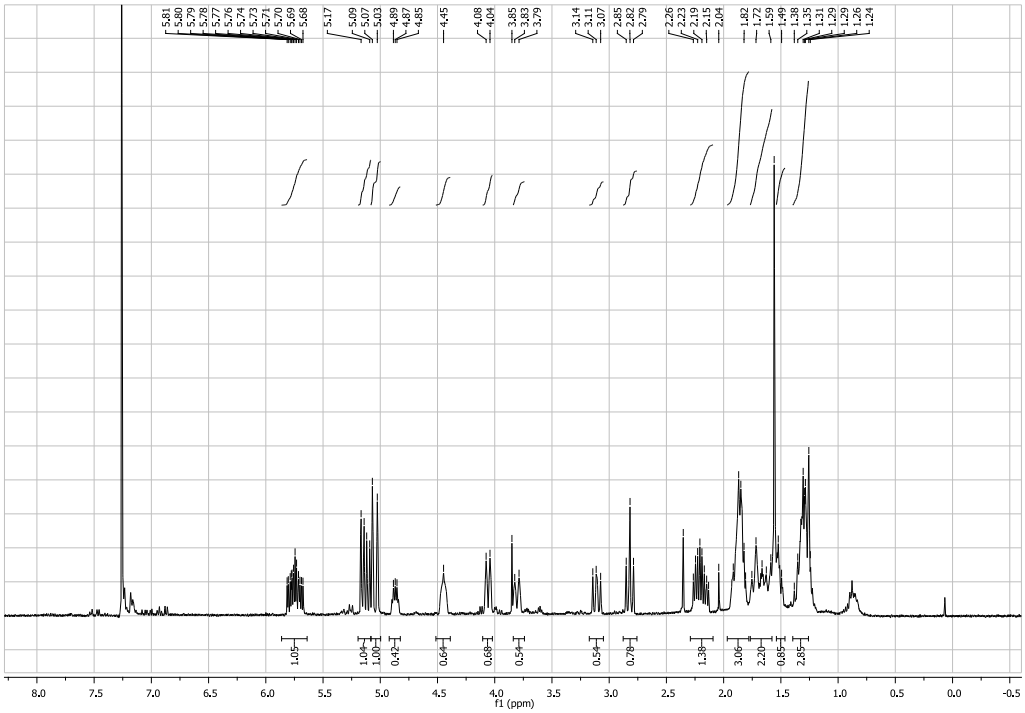
**9**

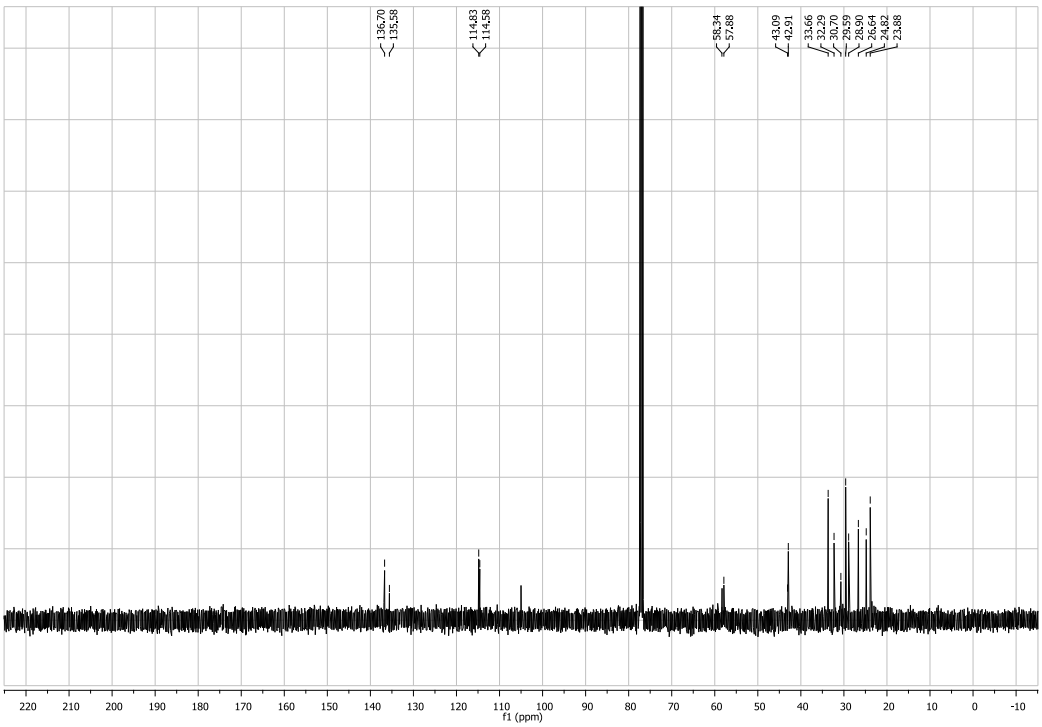

7.26
5.82
5.81
5.80
5.78
5.77
5.77
5.76
5.74
5.33
5.31
5.29
5.26
5.19
5.15
5.11
4.68
4.41
4.38
3.82
3.78
3.27
3.24
3.21
2.94
2.91
2.87
1.92
1.89
1.80
1.79
1.76
1.75
1.71
1.68
1.67
1.66
1.62
1.59
1.55
1.53
1.52
1.51
1.49
1.41
1.40
1.37
1.31
1.29
1.25
0.96
1.10
0.72
1.16
0.37
0.45
0.76
0.74
0.43
1.27
5.57
1.46
f1 (ppm)

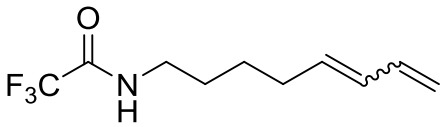

161.94
151.06
135.17
134.63
117.80
117.45
54.79
51.86
42.02
39.19
29.60
28.30
26.03
25.34
19.29
f1 (ppm)


N
CF3
O

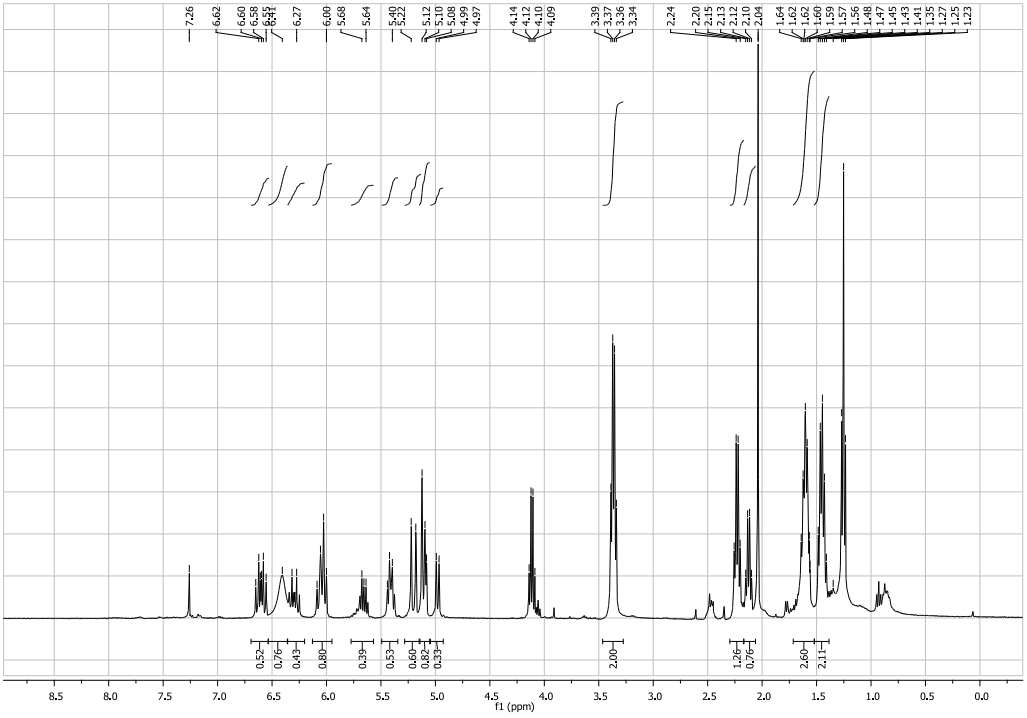
**10**

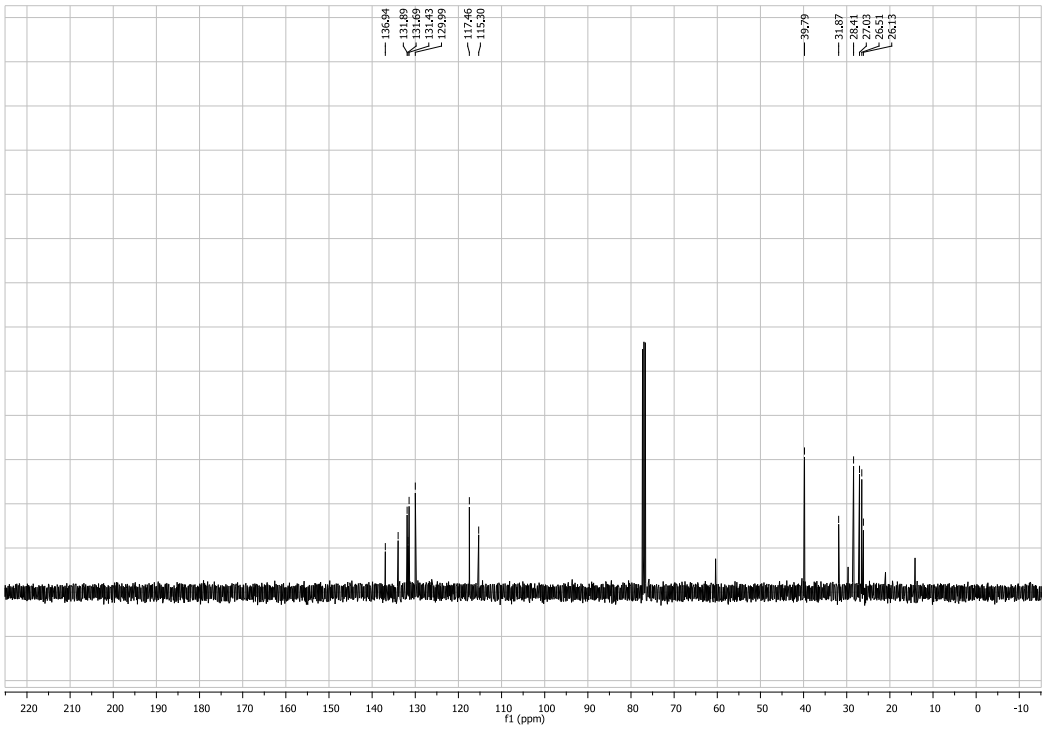

5.81 5.80 5.79 5.78 5.77 5.76 5.74 5.73 5.71 5.70 5.69 5.68 5.17 5.09 5.07 5.03 4.89 4.87 4.85 4.45 4.08 4.04 3.85 3.83 3.79 3.14 3.11 3.07 2.85 2.82 2.79 2.26 2.23 2.19 2.15 2.04 1.82 1.72 1.59 1.49 1.38 1.35 1.31 1.29 1.28 1.26 1.24
1.05 1.04 1.00 0.42 0.64 0.68 0.54 0.54 0.78 1.38 3.06 2.20 0.85 2.85
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

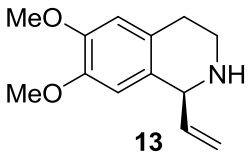

136.70 135.58 114.83 114.58 58.34 57.88 43.09 42.91 33.66 32.29 30.70 29.59 28.90 26.64 24.82 23.88
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



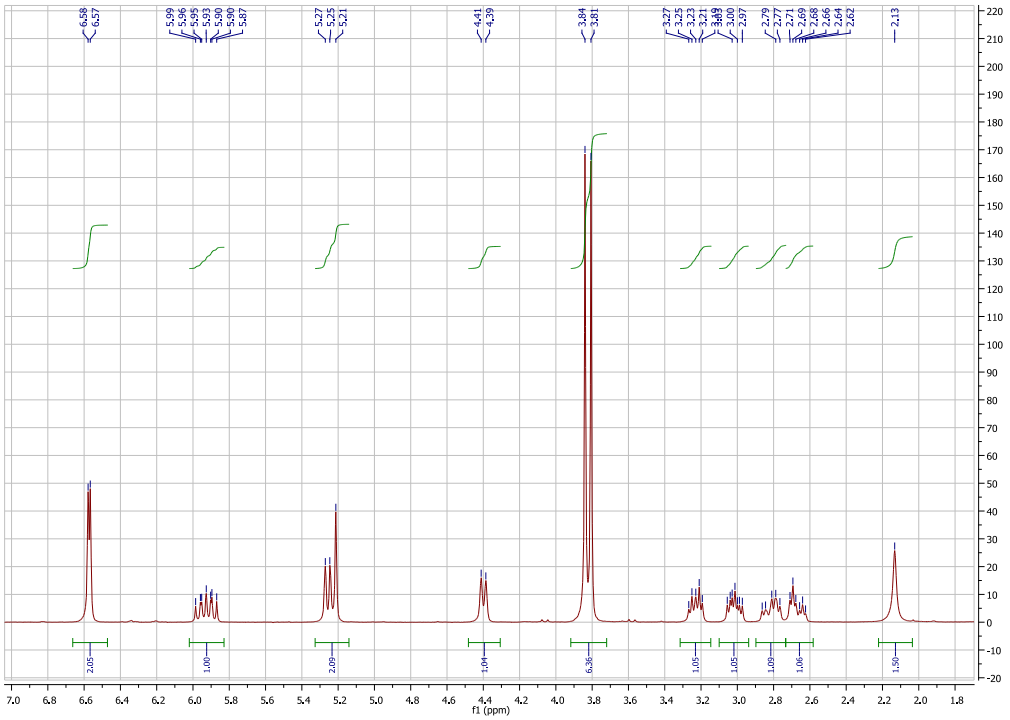
**12**

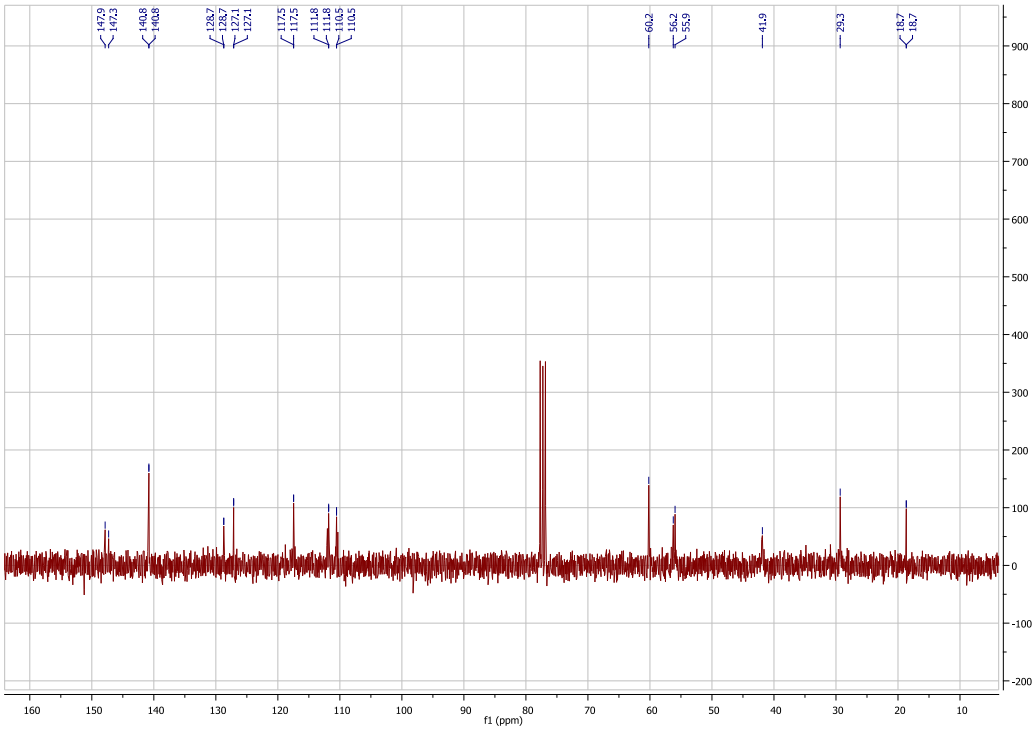

7.26
6.62
6.60
6.58
6.55
6.41
6.27
6.00
5.68
5.64
5.40
5.22
5.12
5.10
5.08
4.99
4.97
4.14
4.12
4.10
4.09
3.39
3.37
3.36
3.34
2.24
2.20
2.15
2.13
2.12
2.10
2.04
1.64
1.62
1.62
1.60
1.59
1.57
1.56
1.48
1.47
1.45
1.43
1.41
1.35
1.27
1.25
1.23
0.52
0.76
0.43
0.80
0.39
0.53
0.60
0.82
0.53
2.00
1.26
0.76
2.60
2.11
f1 (ppm)

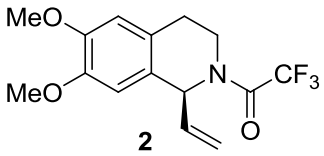

136.94
131.89
131.69
131.43
129.99
117.46
115.30
39.79
31.87
28.41
27.03
26.51
26.13
f1 (ppm)


MeO
MeO
NH

**13**

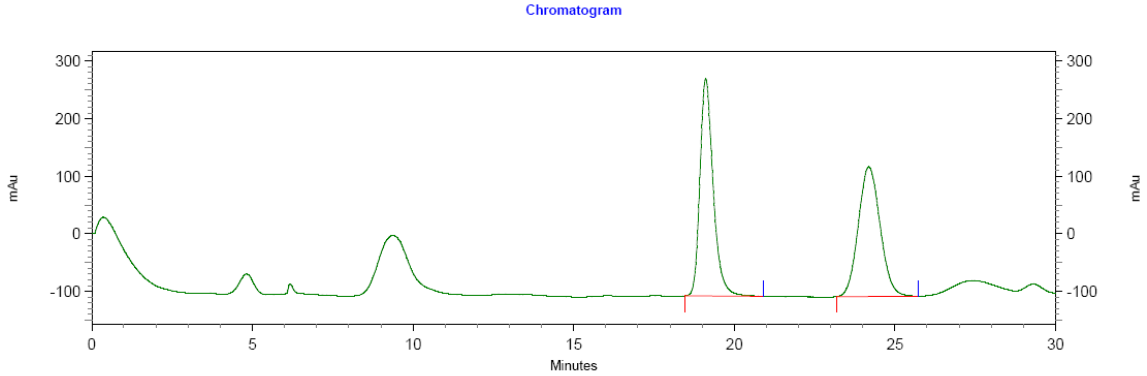

6.58
6.57
5.99
5.96
5.95
5.93
5.90
5.90
5.87
5.27
5.25
5.21
4.41
4.39
3.94
3.81
3.27
3.25
3.23
3.21
3.19
3.00
2.97
2.79
2.77
2.71
2.69
2.68
2.66
2.64
2.62
2.13
2.05
1.00
2.09
1.04
6.36
1.05
1.05
1.09
1.06
1.50
f1 (ppm)


147.9
147.3
140.8
140.8
128.7
128.7
127.1
127.1
117.5
117.5
111.8
111.8
110.5
110.5
60.2
56.2
55.9
41.9
29.3
18.7
18.7
f1 (ppm)




**2**

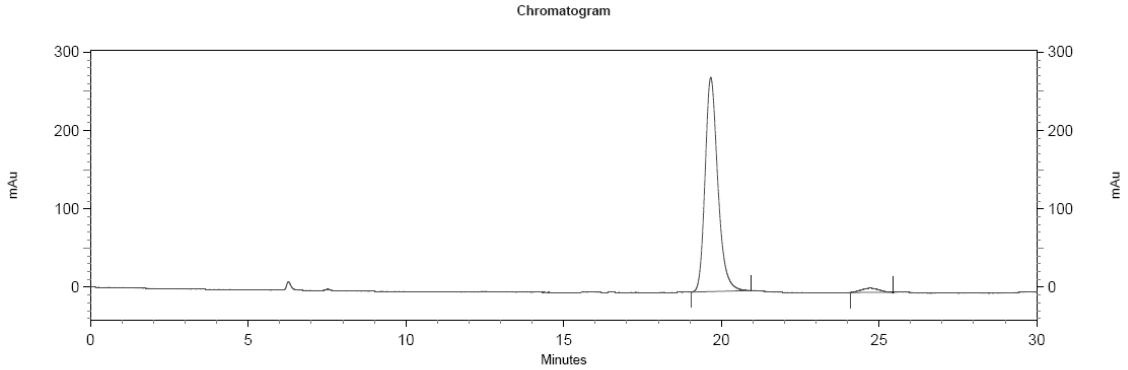
racemic




1: 210
nm, 2 nm
Results

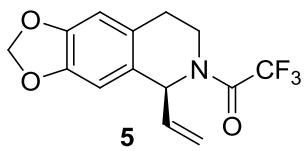
| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 19,112 Minutes | 19,112 | 10822371 | 50,454 |
| 2 | Peak @ 24,188 Minutes | 24,188 | 10627775 | 49,546 |

Chiral



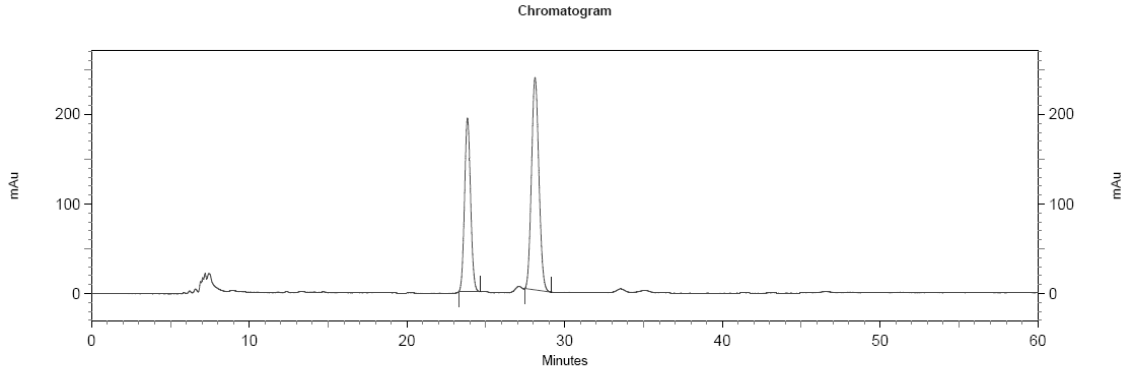

1: 210
nm, 2 nm
Results

| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 19,664 Minutes | 19,664 | 7679923 | 97,301 |
| 2 | Peak @ 24,720 Minutes | 24,720 | 213005 | 2,699 |




**5**

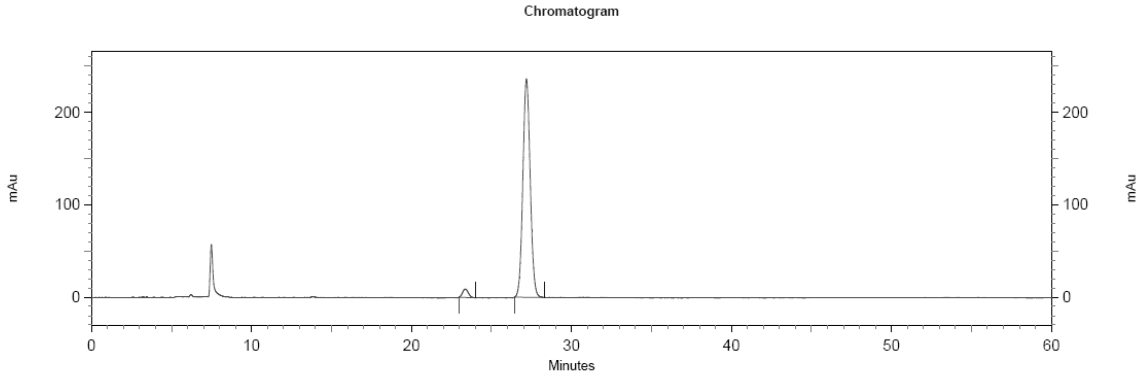
Racemic




1: 210 nm,
2 nm Results

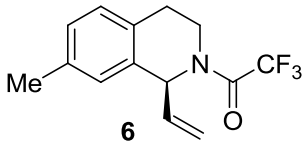
| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 23,836 Minutes | 23,836 | 5155858 | 39,911 |
| 2 | Peak @ 28,120 Minutes | 28,120 | 7762579 | 60,089 |

Chiral



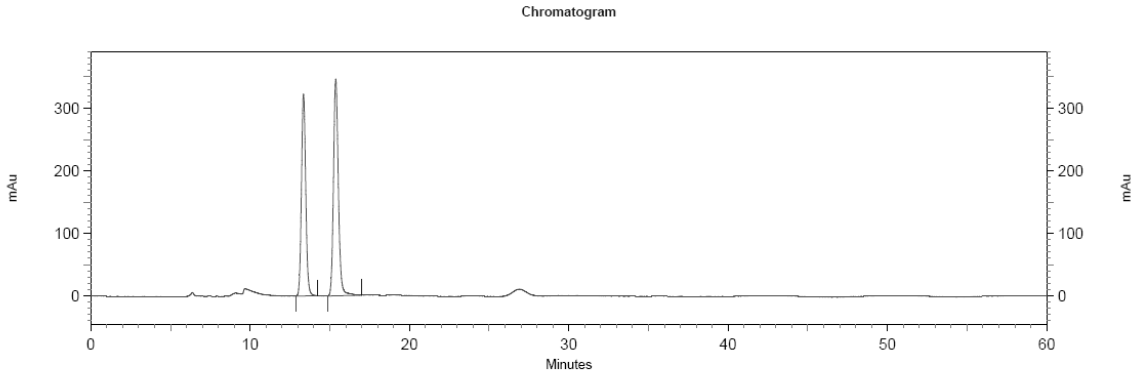

1: 210 nm,
2 nm Results

| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 23,364 Minutes | 23,364 | 230181 | 2,971 |
| 2 | Peak @ 27,184 Minutes | 27,184 | 7518676 | 97,029 |




**6**

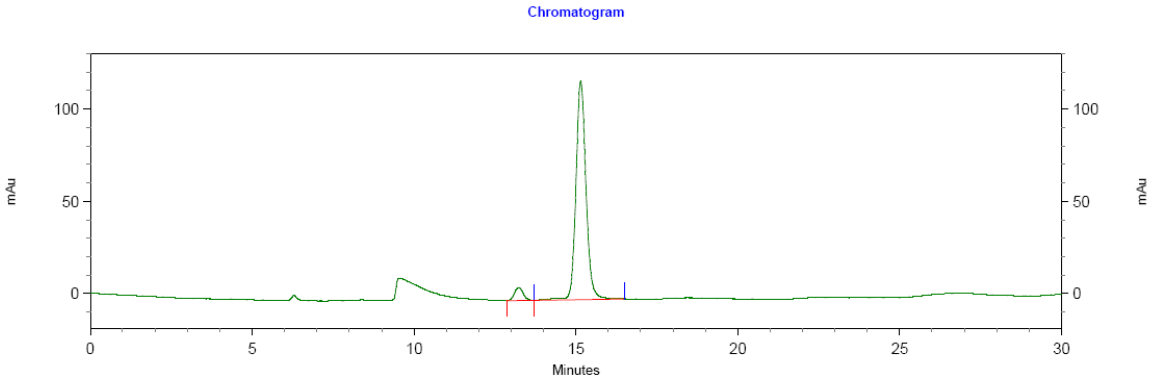
Racemic




1: 210
nm, 2 nm
Results

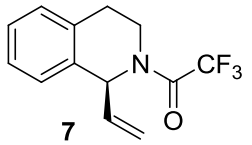
| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 13,348 Minutes | 13,348 | 6035841 | 45,059 |
| 2 | Peak @ 15,372 Minutes | 15,372 | 7359446 | 54,941 |

Chiral



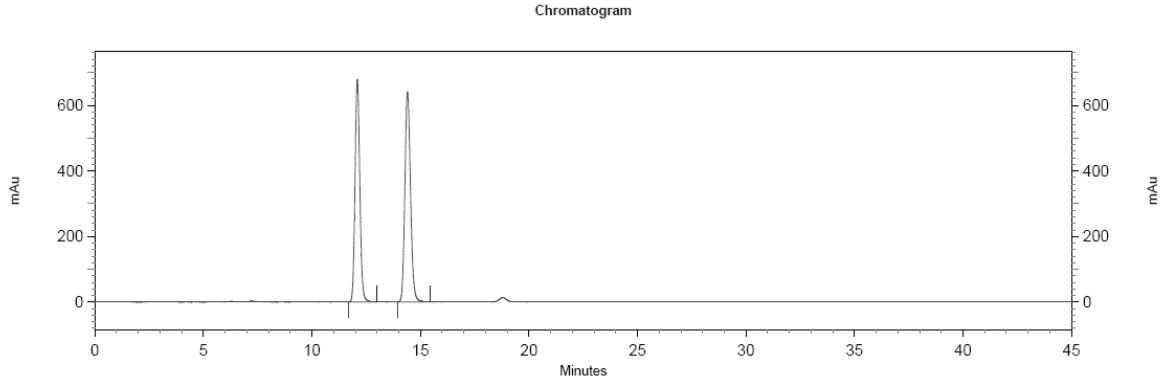

1: 210
nm, 2 nm
Results

| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 13,232 Minutes | 13,232 | 131910 | 4,904 |
| 2 | Peak @ 15,152 Minutes | 15,152 | 2557931 | 95,096 |




**7**

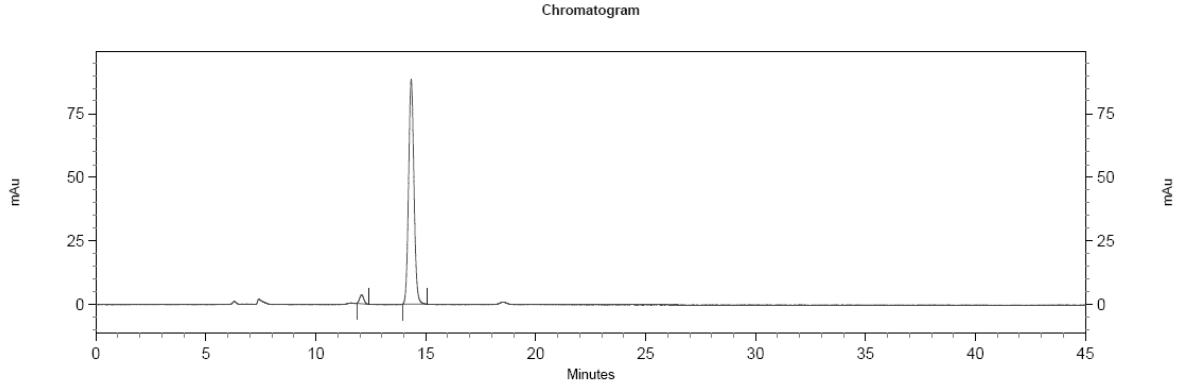
Racemic




1: 220
nm, 2 nm
Results

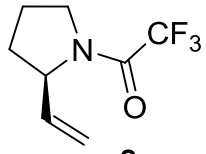
| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 12,092 Minutes | 12,092 | 10392779 | 47,377 |
| 2 | Peak @ 14,404 Minutes | 14,404 | 11543693 | 52,623 |

Chiral



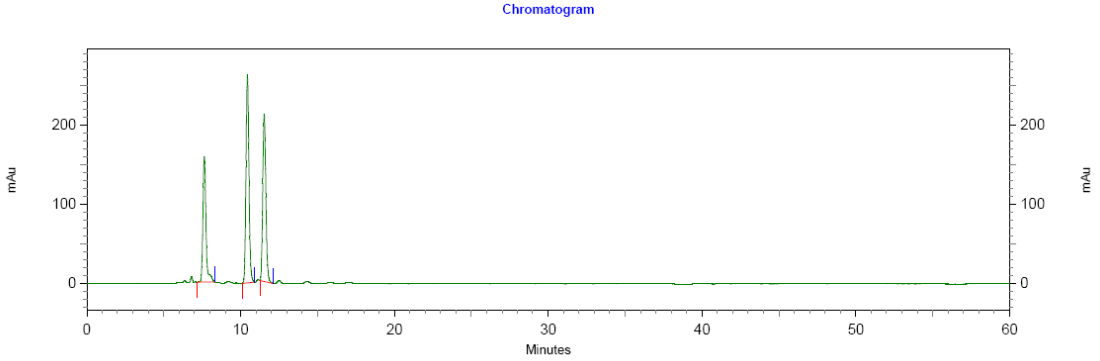

1: 220
nm, 2 nm
Results

| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 12,088 Minutes | 12,088 | 46727 | 3,024 |
| 2 | Peak @ 14,336 Minutes | 14,336 | 1498323 | 96,976 |




**8**

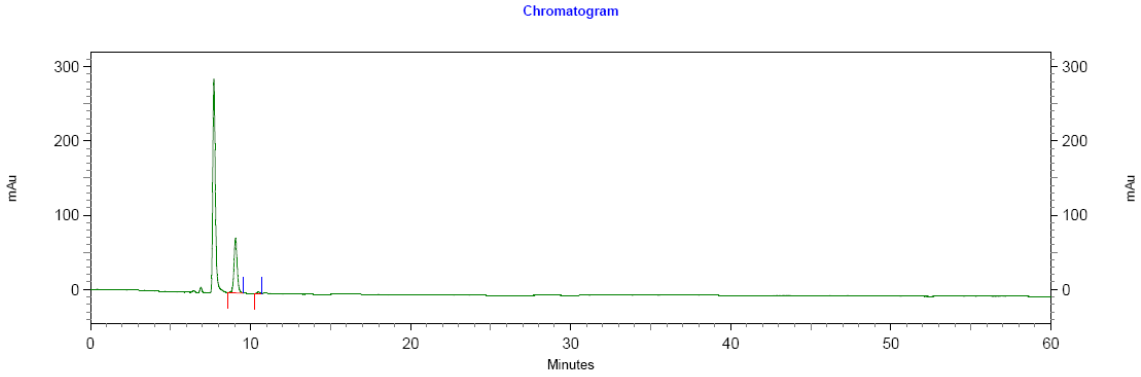
racemic




1: 210 nm,
2 nm Results

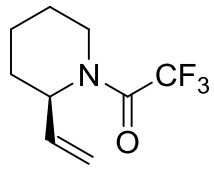
| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 2 | Peak @ 10,444 Minutes | 10,444 | 3499053 | 40,748 |
| 3 | Peak @ 11,536 Minutes | 11,536 | 2937285 | 34,206 |

chiral



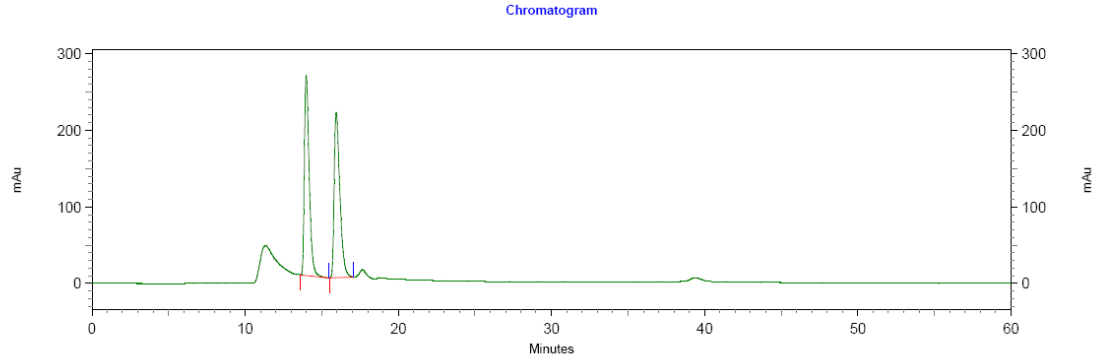

1: 210 nm,
2 nm Results

| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 9,068 Minutes | 9,068 | 1002093 | 97,961 |
| 2 | Peak @ 10,492 Minutes | 10,492 | 20860 | 2,039 |




**9**

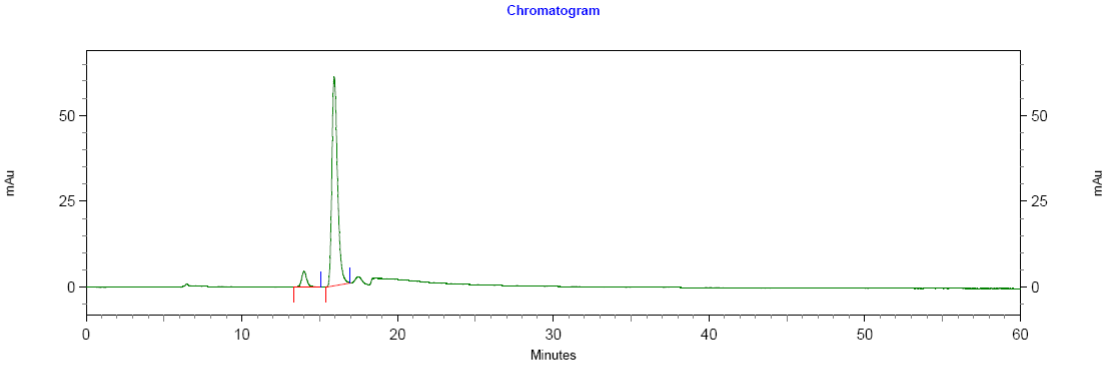
Racemic




1: 230
nm, 4 nm
Results

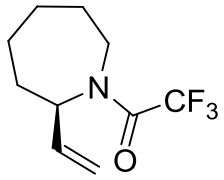
| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 13,988 Minutes | 13,988 | 5671031 | 50,379 |
| 2 | Peak @ 15,952 Minutes | 15,952 | 5585760 | 49,621 |

chiral



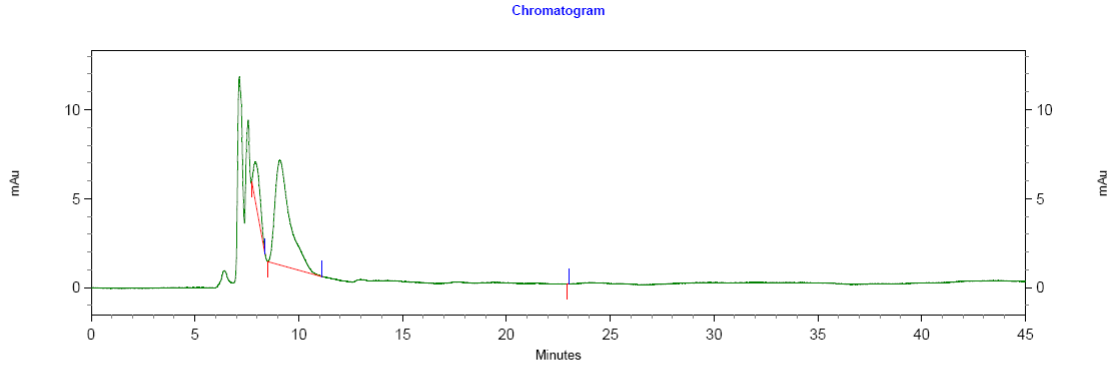

1: 230
nm, 4 nm
Results

| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 14,000 Minutes | 14,000 | 108426 | 6,599 |
| 2 | Peak @ 15,936 Minutes | 15,936 | 1534639 | 93,401 |




**10**

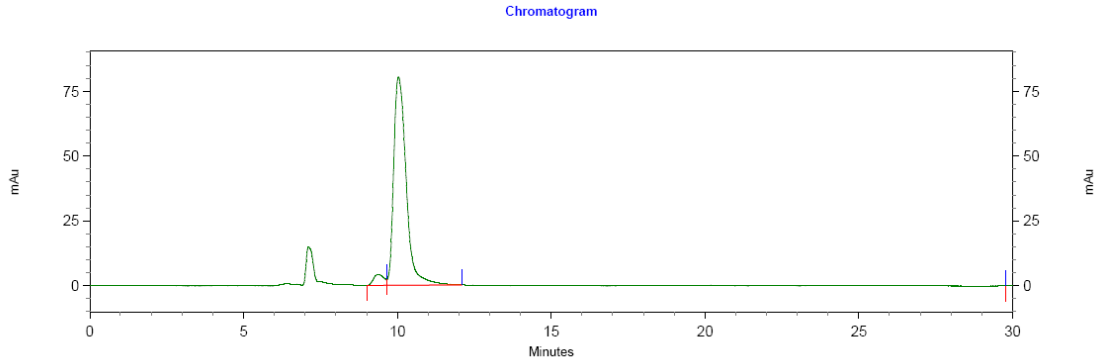
Racemic




1: 220
nm, 4 nm
Results

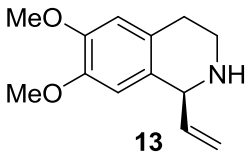
| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 7,920 Minutes | 7,920 | 53115 | 15,233 |
| 2 | Peak @ 9,092 Minutes | 9,092 | 295500 | 84,747 |

Chiral




1: 220
nm, 4 nm
Results

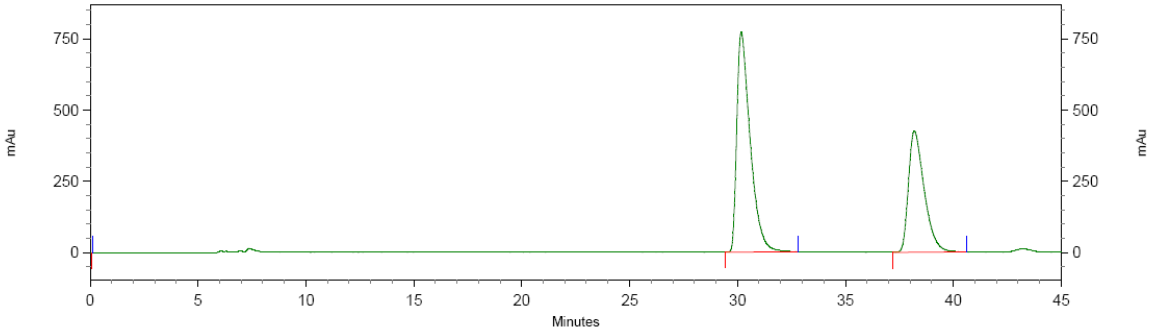
| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 9,376 Minutes | 9,376 | 98646 | 4,158 |
| 2 | Peak @ 10,040 Minutes | 10,040 | 2273778 | 95,842 |




**13**

Racemic

Chromatogram

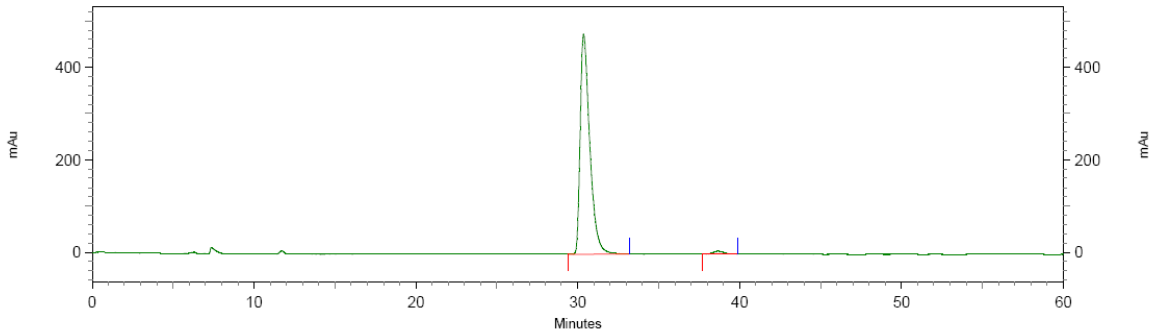



1: 210
nm, 2 nm
Results

| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 2 | Peak @ 30,172 Minutes | 30,172 | 33418698 | 60,749 |
| 3 | Peak @ 38,196 Minutes | 38,196 | 21591978 | 39,251 |

Chiral

Chromatogram




1: 210
nm, 2 nm
Results

| Pk # | Name | Retention Time | Area | Area Percent |
|---|---|---|---|---|
| 1 | Peak @ 30,364 Minutes | 30,364 | 19590268 | 98,393 |
| 2 | Peak @ 38,672 Minutes | 38,672 | 320024 | 1,607 |